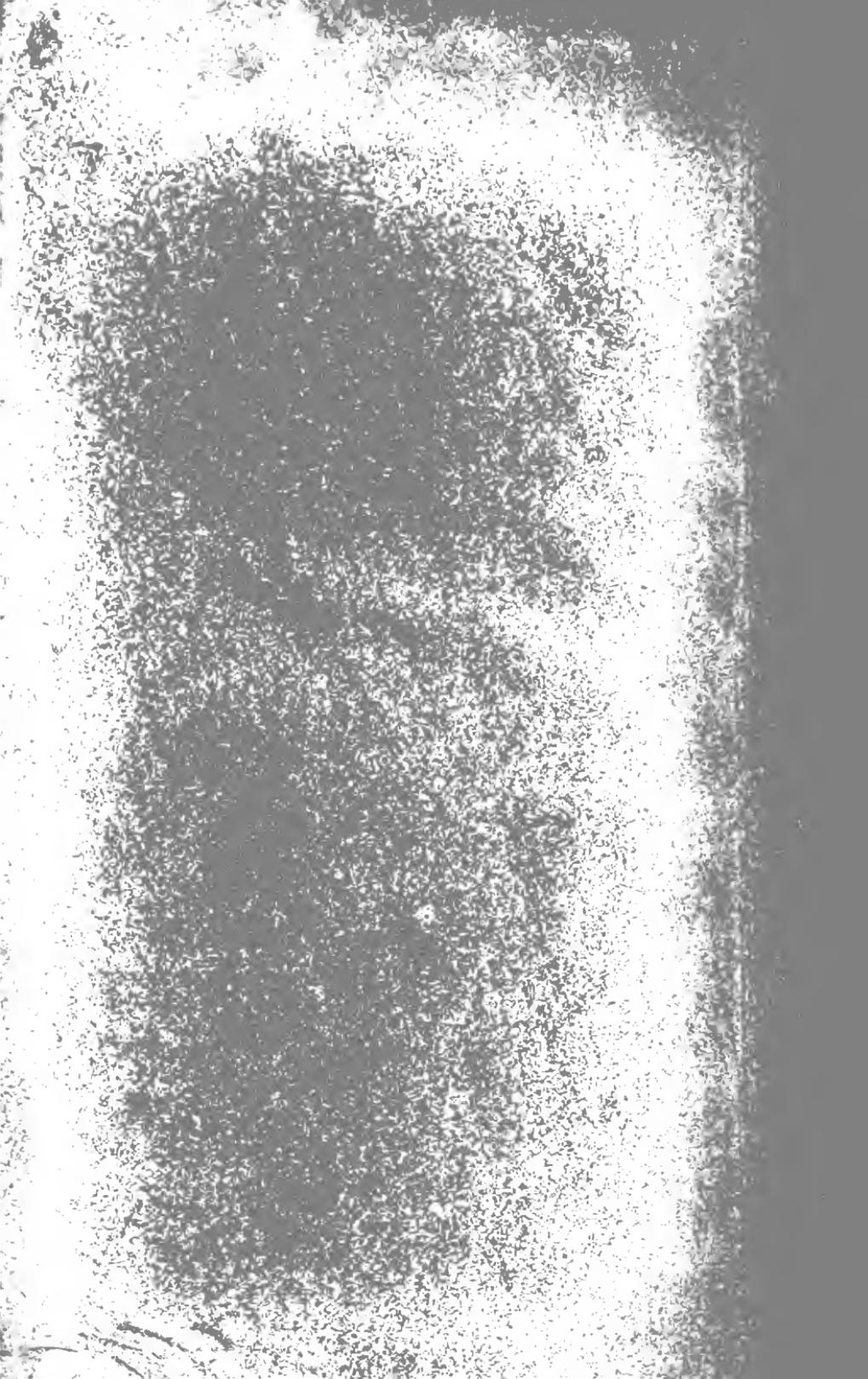
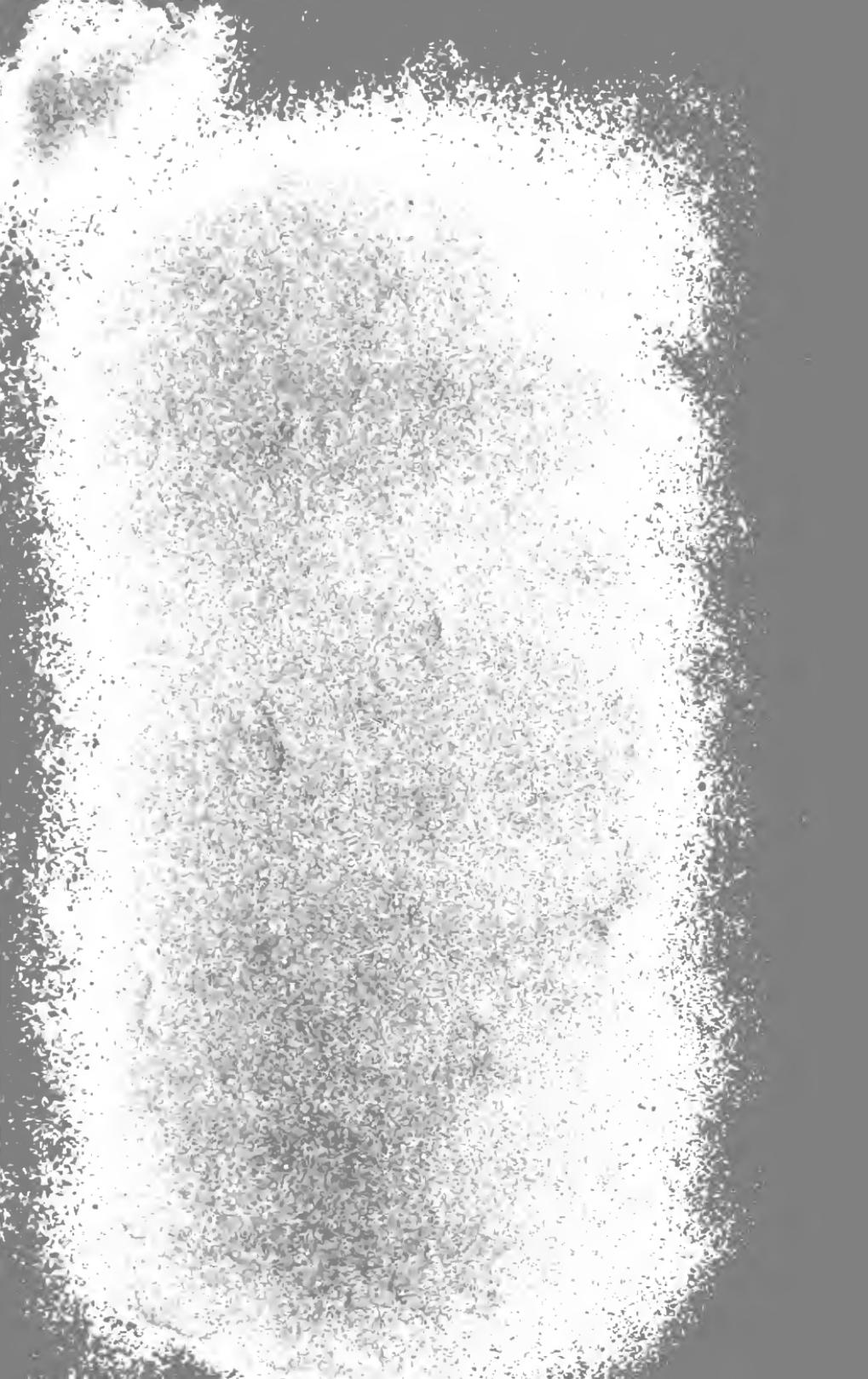




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# INTRODUCTION TO CHEMICAL-TECHNICAL ANALYSIS

BY

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IN VIENNA

(AUTHORIZED TRANSLATION)

WITH APPENDIX BY THE TRANSLATOR

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*ILLUSTRATED*

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## Preface.

IT is generally conceded that it is advisable to give students of chemistry as broad an experience as possible in the use of analytical methods, in order to have them acquire skill in manipulation and to acquaint them with the important bearing of chemical analysis.

This experience can, in a great measure, be obtained by supplementing the usual preparatory courses in gravimetric and volumetric analysis with instruction in the execution of methods which are being constantly applied in the analysis of industrial products. The authors of this book have had much experience in teaching chemical-technical analysis, and in the following pages have presented many methods of this description in a series of examples, selected from a variety of products. They have been very fortunate in their choice, and have undoubtedly done much to assist the earnest student.

The conviction that a course of this character would be welcomed by English-speaking students, and helpful not only to them but also to many who are already engaged in industrial pursuits, has led the translator to publish the little volume in its present form. He has not edited the text, but has taken the liberty to add an appendix, in which are incorporated additional examples which actual laboratory testing has shown to be highly instructive, as well as exceedingly valuable, in the direction of imparting skill in manipulation.

In this connection, too, the translator would take occasion to acknowledge his great indebtedness to Mr. Walter T. Taggart, B. S., for valuable assistance rendered in the reading of the proof and the preparation of the index.

H. F.

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**Abbreviations.**

Bé. = Beaumé.

c.c. = Cubic Centimeter.

C. = Celsius.

Conc. = Concentrated.

F. = Fahrenheit.

Gr. = Gram.

m.m. = Millimeter.

Temperature (Celsius is understood unless otherwise indicated.)



# I. Products of Technical Chemistry.

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In this chapter a selection is made from the most important industrial chemical products as well as from the raw materials used therein, and a description of the quantitative examination of the same is given. The methods described are followed by those employed in the analysis of water, coal and furnace gas.

## 1. Iron Pyrites.

The most important determination is that of sulphur. The error must not exceed .1 per cent. In addition a water determination is usually conducted, and less frequently estimations of copper and arsenic.

(a) Sulphur. Following the method of Lunge, which is adopted in the German Le Blanc soda factories, .5 gram of finely-divided and bolted pyrite is covered with 10 c.c. of a mixture of 3 vols. nitric acid (sp. gr. 1.4) and 1 vol. fuming hydrochloric acid in an Erlenmeyer flask. A funnel is inserted and the contents are warmed until reaction begins. The flask is then removed from the water-bath, and the reaction proceeds of its own accord until nearly complete. The contents are warmed anew until the reaction is finished. Solution takes place in about ten minutes. Only small quantities of colorless substances, silica, barium sulphate, lead sulphate, etc., but neither dark particles nor sulphur, may remain undissolved. The solution is evaporated to dryness in a porcelain dish with an excess of hydrochloric acid; the residue is moistened with a few drops of hydrochloric acid, taken up with hot water, and filtered. In the filtrate, at a temperature of 60–70° the iron is precipitated with a slight excess of ammonia. The precipitate is thrown on a sufficiently porous filter and washed with hot water until 1 c.c. filtrate remains perfectly clear for several minutes on addition of barium chloride solution. The filtrate is acidified with hydrochloric acid, brought to boiling, and the sulphuric acid is

precipitated with about 20 c.c. of a hot solution of barium chloride (10 per cent.). The remainder of the analysis is conducted in the usual manner. The sulphur in pyrite varies between 46 and 52 per cent. Spanish and Norwegian pyrites are characterized by their high percentage of sulphur.

(b) Moisture. About 10 grs. sample are dried to constant weight in an air-bath at 105°. Usually four hours are required for this operation.

(c) Copper. According to the procedure of Duisberger-Hütte,\* five grams of the finely-ground and previously dried (100°) mineral are gradually brought into an inclined Erlenmeyer flask containing 60 c.c. nitric acid (sp. gr. 1.2). As soon as the ensuing violent reaction ceases the flask is heated and the contents are evaporated until sulphuric acid vapors are evolved. The dry residue is then dissolved in 50 c.c. HCl (sp. gr., 1.19), 2 grams sodium hypophosphite dissolved in 5 c.c. water are added, and the liquid is boiled to remove the arsenic and reduce the iron. An excess of concentrated HCl is now added, followed by 300 c.c. hot water, and hydrogen-sulphide gas to saturation. The precipitate is filtered off and thoroughly washed. The filter is broken with a glass rod, and the contents are washed back into the precipitates in flask. The adhering particles on the filter, together with the main portion of the precipitate, are dissolved in nitric acid and the solution is evaporated to dryness on a water-bath. The residue is treated again with nitric acid and water, neutralized with ammonia, and a slight excess of dilute sulphuric acid is added. After cooling, the solution is filtered, the flask and filter are washed with water containing sulphuric acid, and the copper is determined electrolytically in the filtrate after adding 3 to 8 c.c. nitric acid, or gravimetrically without the addition of nitric acid as cuprous sulphide. From the percentage found, .01 is deducted for bismuth and antimony. Any appreciable amount of copper in pyrite is easily recognized during the sulphur determination by the blue ammoniacal filtrate.

(d) Arsenic. (Method of Reich, modified by McCay.) 0.5 gram of pyrite is dissolved in a porcelain crucible with nitric acid. The free acid is volatilized, 4 grams soda are added, and the mass is

\* Taschenbuch für die Soda-, Pottasche- und Ammoniaksfabrikation von Dr. G. Lunge. 2 Aufl.

thoroughly dried on a sand-bath, when 4 grams saltpetre are added and the contents are heated to quiet fusion for ten minutes. The fusion is lixiviated with a small quantity of hot water, and to the filtered solution sufficient nitric acid is added to slightly acidify, after which the liberated carbonic acid is expelled by boiling. Silver nitrate is now added, and the solution is carefully neutralized with weak ammonia. All arsenic is obtained in the form of silver arsenate, which is dissolved in dilute nitric acid. The solution is either evaporated in a platinum capsule, dried and weighed as silver arsenate ( $\text{Ag}_3\text{AsO}_4$ ), or titrated with ammonium sulpho-cyanide according to the method of Volhard.

## 2. Pyrite Residuum.

The determination of sulphur in pyrite residuum, an operation not infrequently required, can be carried out under the directions given in Example 1, except that, in order to avoid evolution of hydrogen sulphide, solution is advantageously effected by nitric acid and only a few drops of hydrochloric acid.

Lunge\* recommends for this purpose the following method :

Exactly 2 grams of sodium-bicarbonate, whose strength has been previously estimated by titration, are thoroughly mixed with 3.2 grams finely-divided residuum in a nickel crucible of about 30 c.c. capacity. The mixture is heated first for 10 minutes with a small flame just touching the bottom, and afterwards for 15 minutes with a strong flame, without allowing the mass to melt. The crucible should be covered during this operation. The contents are poured out into a porcelain dish, the crucible is rinsed with water, and treated for ten minutes with a concentrated neutral brine in order to avoid subsequent escape of iron oxide through the filter. The undissolved portion is filtered off and washed until the filtrate ceases to give an alkaline reaction. After cooling, the liquid is titrated back with normal acid, using methyl-orange as an indicator. The difference between the number of c.c. hydrochloric acid ( $a$ ) necessary to neutralize 2 grs. bicarbonate and the number of c.c. ( $b$ ) used in back titration, multiplied by the sulphur equivalent (1 c.c. in acid = 0.016 gr. S) gives the amount of sulphur

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\* Taschenbuch fur die Soda-fabrikation, etc.

present. Using the above amount of substance, the percentage of sulphur is :

$$S = \frac{a-b}{2}.$$

### 3. Sulphuric Acid.

A quantitative determination of the impurities is seldom made except, for example, for storage-battery purposes. The qualitative tests here given for detection of sulphurous acid, hydrochloric acid, and the oxides of nitrogen, lead, iron and arsenic, are according to the methods of Krauch.

(a) Sulphurous acid. To a weak yellow solution of iodine, previously treated with starch paste, the diluted sulphuric acid is added. In presence of sulphurous acid decolorization takes place. Or the sulphurous acid is reduced with zinc or aluminium to hydrogen sulphide, and the latter detected by means of lead-paper or an alkaline solution of sodium nitroprusside (very delicate).

(b) Hydrochloric acid. Two grams sulphuric acid are diluted to 30 c.c. and a few drops of a silver nitrate solution are added. Presence of hydrochloric acid is indicated by turbidity.

(c) Oxides of nitrogen. A very trustworthy test is the diphenylamine test. This is conducted, according to Wagner, in the following manner : To 1 c.c. pure distilled water in a porcelain capsule, a few crystals of diphenylamine are added, followed successively by two additions,  $\frac{1}{2}$  c.c. each, of the conc. acid under examination. Traces of nitric acid produce a blue coloration after a time. (The same reaction is shown by other oxidizing substances.)

(d) Lead. The acid is mixed with 5 times the volume of strong alcohol. A turbidity after a time indicates the presence of lead sulphate, which is further identified by dissolving the precipitate in ammonium acetate, and testing with potassium chromate or hydrogen sulphide.

(e) Iron. The acid is boiled with a few drops of nitric acid diluted with a little water. It is allowed to cool, and ammonium sulphonyl-cyanide is added. A red tint indicates the presence of iron.

(f) Arsenic. Two grs. conc. sulphuric acid, diluted with an equal volume of water, are warmed with a few pieces of granu-

lated zinc until strong evolution of gas begins. A yellow coloration indicates arsenic. Sulphuric acid may contain as high as 0.1 per cent., and in exceptional cases as high as 0.4 per cent. arsenic. On account of the injurious action of the latter, a quantitative estimation is often desirable. For this purpose the following method of Lunge is recommended :

About 20 grams acid are diluted with an equal volume of water. In order to reduce the arsenic acid present, sulphurous acid is conducted into the liquid for some time, until the odor is pronounced. Heat is applied and carbonic acid is conducted in until the odor disappears, when carbonate of soda is added to exact neutralization, followed by a small quantity of bicarbonate of soda. The liquid is then titrated with  $\frac{1}{10}$  normal iodine solution, using starch solution as indicator. (1 c.c. iodine solution = 0.00495 gr.  $\text{As}_2\text{O}_3$ .) Any appreciable quantity of iron must previously be removed.

### Fuming Sulphuric Acid and Anhydride.

Lately there has appeared in commerce fuming sulphuric acid in form of an oily, thick liquid containing a high percentage of  $\text{SO}_3$  (upward of 70 per cent.), or in form of a solid, which is used principally in the dye industry. Anhydride is a solid mass containing 80-90 per cent. free  $\text{SO}_3$  and 10-20 per cent. monohydrate. The analysis is confined principally to the estimation of anhydride and sulphurous acid. In weighing the substance and subsequently diluting, special care is to be observed in preventing on the one hand the absorption of moisture while weighing, and on the other hand in preventing the volatilization of anhydride and sulphurous acid by the heat produced in diluting. The following procedure recommended by Lunge has been found most advantageous :

The substance is weighed in a thin bulb tube, both ends of which are drawn out to capillaries. The weight of the empty bulb is first ascertained. 3-5 grams of the substance, carefully melted, if necessary, in a sand-bath or iron plate, are drawn into the bulb. To effect this a flask with a narrow neck and a caoutchouc stopper with single perforation is used. Through the stopper a tight-fitting glass tube with stopcock issues, over the end of which a rubber tube is drawn. On applying suction with the mouth to this, and then quickly closing the stopcock, a partial vacuum is produced. The

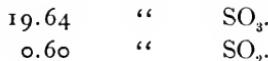
open end of the rubber tube is drawn over the capillary on the bulb, the other end of which is introduced into the liquid to be analyzed. By opening the cock the necessary amount, which, however, should not more than half fill the bulb, is introduced. The capillary is then drawn from the liquid, cleaned, sealed, and weighed in horizontal position. The bulb is now placed open end downward in a small Erlenmeyer flask, whose mouth is closed by the bulb, and which contains sufficient water to deeply immerse the capillary. The sealed end is broken, the liquid is allowed to run out, and the bulb is washed first by washing through the capillary and eventually by drawing water into the entire bulb. When the most concentrated oil (about 70 per cent.) is used, direct addition to water without loss cannot be accomplished. In this case both ends of the bulb, prepared as above, are sealed, and the bulb is introduced into a well-ground glass-stoppered flask, containing considerable water. The flask is shaken to break the bulb, and afterwards allowed to stand. The contents of the flask are poured into a graduated flask, diluted to 500 c.c. exactly, and in one portion the total acid is estimated by alkali, while in another the sulphurous acid is titrated with iodine solution.\* In the calculation, the result of the titration with caustic soda is expressed in per cent. sulphuric anhydride (a), and that of titration with iodine solution in per cent. sulphurous anhydride (b). The value of (b) is transformed into sulphuric anhydride, and the value (c) so obtained subtracted from a; the difference (a-c) then represents the total amount of sulphuric anhydride. Moreover, if the sum (a-c)+b be subtracted from 100, the quantity of water of hydration can be ascertained, and the monohydrate present can be calculated in percentage (d). The difference 100-(d+b) yields the percentage of free active anhydride.

*Example.*—In the examination of a sample of fuming sulphuric acid the result of the titration with alkali showed 85.5 per cent. SO<sub>3</sub> (a), the titration with iodine 0.6 per cent. SO<sub>2</sub> (b). The value b is changed to SO<sub>3</sub> by the proportion 64:80=0.6:c, and from this c is found to equal 0.75 per cent. The difference a-c=84.75 per cent. SO<sub>3</sub>. The sum (a-c)+b=85.35 per cent., which

\* In weighing, the stopcock bulb pipettes of Lunge and Rey may also be used to advantage.

subtracted from 100 gives 14.65 per cent. water of hydration. This, according to the proportion 18 : 98 = 14.65 : d, corresponds to d = 79.76 per cent. monohydrate. There remains, therefore,  $100 - (d+b) = 100 - 80.36 = 19.64$  per cent. sulphuric anhydride.

The acid contains, therefore, 79.76 per cent.  $H_2SO_4$ ,



If the fuming sulphuric acid contains no sulphurous acid, the difference 100-a yields the percentage of water of hydration. The quantity of monohydrate corresponding to this value is obtained from the proportion 18 : 98 : : (100-a) : d, and from the difference 100-d the amount of free anhydride is found.

#### Nitroso Acid (Nitrated Acid).

The proportion of total compounds of nitrogen in nitroso acid, a question of great importance in the lead-chamber process, is estimated by means of the Lunge nitrometer. The estimation depends on the fact that the acids containing nitrogen, which are dissolved in the sulphuric acid, are reduced by contact with metallic mercury to NO, the amount of which is determined. The nitrometer in its original form presents the following arrangement: The tube (*a*) (Figure 1), divided in  $\frac{1}{5}$  or  $\frac{1}{10}$  c.cm., is provided with a cup above and has a capacity upward of 50 c.c. Directly below the cup is a three-way cock, whose straight opening establishes communication with the eudiometer, while a second indirect opening allows the contents of the cup to empty through the axis of the stopcock. For this purpose a rubber tube, provided with a screw clamp and a glass tube, is fastened to the stopcock. Finally, the cock can be placed so that the cup communicates with neither opening.

The tube (*b*) is made of strong glass tubing of nearly the same diameter and capacity as (*a*). Both tubes are attached to a stout rubber tube. The remainder is self-evident. During manipulation the tube (*b*) is so adjusted that the lower end is somewhat above the stopcock of (*a*), which is then opened; mercury is poured into (*b*) until the level enters the cup. Since the mercury enters (*a*) from below, no air-bubbles collect on the glass walls. The cock is closed, the mercury run out of the cup through the side-

opening, the tube (*b*) is lowered, and the cock is adjusted to cut off all communication.

The nitroso acids are now run into the cup from a very small pipette (the stronger acids require 0.5 c.c., the weaker 2-5 c.c.), and the level in the tube (*b*) is lowered somewhat. The cock is opened, and the acid is allowed to drain into tube (*a*), care being taken to admit no air. The cup is then rinsed in the same manner twice, first with 2-3 c.c., and again with 1-2 c.c. absolutely nitroso free, concentrated sulphuric acid.

The entire volume of acid introduced should not exceed 8-10 c.c. Gas evolution is started by removing the tube (*a*) from its clamp, placing it in an almost horizontal position and suddenly righting a number of times to insure thorough mixture of acid and mercury. It is then shaken for 1-2 minutes until gas evolution ceases. Usually this time suffices. It is allowed to stand until the acid clears, cools off, and the foam disappears, an operation which lasts but a short time. The tube (*b*) is raised to bring the mercury level sufficiently above that in (*a*) to correspond to the volume of sulphuric acid in the latter (for

every 7 mm. acid 1 mm. mercury), after which the volume of nitric oxide, which should never exceed 50 c.c., is read off, reduced to 0° C. and 760 mm. pressure. The calculation of the amount of nitrous oxide is simple, since every c.c. reduced volume equals 1.701 mg.  $N_2O_3$ . Any nitric acid present is thereby also reckoned as  $N_2O_3$ .

Lunge has prepared tables by means of which the reduced volume, as well as the amount of nitroso acid, may be read off directly. If it should be found desirable, after reading, to ascertain whether the acid column in the eudiometer is compensated for by the



FIG. 1.—Lunge's Nitrometer.

mercury column in (*b*), the stopcock is opened. Should the level of the acid rise, the pressure was too great. Should it fall, however, the pressure was insufficient. Hence the volume read was in the first instance too small, in the second instance too large. Given, for example, 15.3 c.c., should the acid rise to 15.2 on opening the stopcock, the corrected volume would equal  $15.3 + 0.1 = 15.4$  c.c.

The apparatus is prepared for a new determination by opening the cock and raising the tube (*b*), thereby forcing out the nitric oxide which enters the cup, followed by the acid containing suspended mercurous sulphate. The moment mercury enters the cup the stopcock is closed and the acid is allowed to issue through the axial perforation. The final traces are removed from the cup with filter-paper, after which the stopcock is re-arranged to prevent communication either way.

Should a nitroso acid contain an appreciable quantity of sulphurous acid, it is necessary to add to the same in the cup a quantity of potassium permanganate.

The new gasvolumeter of Lunge is preferable to the original nitrometer. It differs from the latter principally in that the decomposition of the nitroso acids and the measurement of the gas volume formed do not take place in the same tube, but in separate parts of the apparatus. Further, temperature and pressure readings, as well as the involved calculations, are eliminated in reading the gas volume, and finally the apparatus is useful in a number of other analytical operations.

As seen in the accompanying illustration (Fig. 2), the one part of the apparatus—the reaction vessel, consisting of tubes (*E*) and (*D*), the stopcock (*f*) and the cup (*d*)—is very similar to that of the original nitrometer. It differs therefrom, however, in that the tube (*D*), used for decomposing the acid, is not graduated, and the

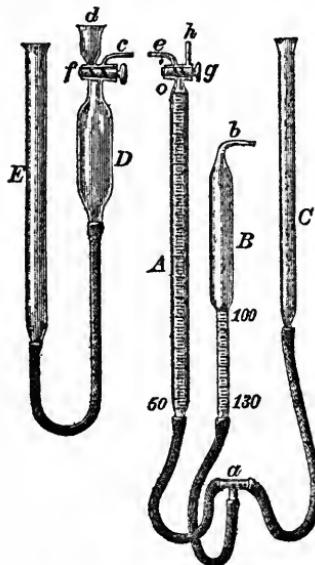


FIG. 2.—Lunge's Gasvolumeter.

stopcock possesses, instead of an axial perforation, a second side-perforation, which establishes communication between the small tube (*c*) and the tube (*D*). In this part of the apparatus the decomposition of the acid is carried out exactly as before. The second part of the apparatus consists of three tubes (*A*), (*B*), and (*C*), which are connected with each other by means of a three-way tube. (*A*) is a glass measuring tube of 50 c.c. capacity, graduated in  $\frac{1}{10}$  c.c. and provided with the double-bored stopcock (*g*), which establishes communication of (*A*) with the straight tube (*h*), as well as with the rectangular tube (*e*). (*B*) serves as a reduction tube. Under the wide portion, which has a capacity of 100 c.c., the tube, to the extent 100 c.c. to 125 c.c., is divided in  $\frac{1}{10}$  c.c., and is filled exactly with so much air that the volume of the latter at  $0^\circ$  and 760 mm. when dry amounts to 100 c.c. The volume *V*, which represents the space which 100 c.c. air at  $0^\circ$  and 760 mm. pressure would occupy at the observed temperature *t* and the pressure *b*, is found by the following equation:  $V = \frac{100 (273+t) 760}{273b}^*$ . One drop of conc. sulphuric acid

is now introduced into (*B*); mercury is poured in the tube (*C*) until the mark in (*B*), representing the volume *V*, is reached, when it is closed by either carefully sealing the latter, care being taken not to warm (*B*), or by closing a previously attached tight-fitting stopcock. The decomposition of the nitroso acid is then carried out in the reaction tube as previously described, and after (*A*) has been filled completely with mercury to the end of the small tube (*e*), by raising (*C*), the tubes (*D*) and (*A*) are placed side by side and (*C*) is connected by means of a rubber tube with (*e*) in such a manner that the two touch each other glass to glass without enclosing air between them. (*E*) is then raised, (*C*) is lowered, the stopcocks (*f*) and (*g*) are opened, and at the moment that the pressure has driven all the gas over into (*A*) and the acid issues from (*D*) through (*c*) and (*e*) to the stopcock (*g*), the latter is closed, together with (*f*), and (*D*) and (*A*) are disconnected. (*C*) is now raised until the mercury in (*B*) rests at precisely 100. By

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\* In very exact determinations, 1 mm. is subtracted for values of *t* up to  $12^\circ$ ; 2 mm. for values from  $13-19^\circ$ , and 3 mm. for values from  $20-25^\circ$ , to allow for expansion of the mercury.

means of a double clamp-holder (*C*) and (*B*) are moved up or down in concert until the mercury in (*A*) and (*B*) reaches the same level, but simultaneously, however, remains at 100 in (*B*). Since the gas in (*B*) is so far compressed as to occupy the same volume as at 0° and 760 mm. pressure, the readings in (*A*) represent the gas reduced to the same normal condition. The temperature in (*A*) and (*B*) is supposed to be the same, a condition quickly produced by the mercury. Ten minutes are required before the final adjustment of the apparatus, when large quantities of nitric oxide are used. By the use of these particular reaction tubes, the inconveniences of foam and slime and the compensation for an acid column are avoided. The eudiometer remains clean, in consequence of which a large number of determinations can be undertaken without constant cleaning.

### 6. Brine.

The following determinations are usually carried out:

Specific gravity, total chlorine, sulphuric acid, ferric oxide, alumina, lime, magnesia, and carbonic acid. In addition, qualitative tests for potassium, bromine and iodine are made, and sometimes these constituents are determined quantitatively.

(*a*) Specific gravity. This is determined by means of the pyknometer in the usual manner.

(*b*) Total chlorine. 10 c.c. brine are diluted to 1000 c.c. A gravimetric or volumetric determination of chlorine in 25 c.c. is made.

(*c*) Sulphuric acid. To 50 c.c. brine a few drops of hydrochloric acid are added. (Sodium chloride is precipitated in this instance from the very concentrated brine solution.) One to two volumes of water are added, and the hot solution is precipitated with barium chloride.

(*d*) Ferric oxide and alumina. 250 c.c. brine, previously heated with a small quantity of nitric acid, are precipitated after addition of ammonium chloride with ammonia. The precipitate, of which there is usually a small quantity, is filtered, and both constituents are weighed together. The presence of iron can be ascertained previously in a separate portion of the brine, oxidized with nitric acid, by the addition of ammonium sulpho-cyanide.

(e) Lime is precipitated with ammonium oxalate in the filtrate from *d*. The precipitate is treated in the usual manner.

(f) Magnesia. To the filtrate from the lime sodium hydrogen phosphate is added. The precipitate which forms is weighed as magnesium pyrophosphate.

(g) Carbonic acid. 1-2 drops methyl-orange are added to  $\frac{1}{2}$  liter brine. The solution is then titrated with  $\frac{1}{10}$  normal hydrochloric acid to red coloration. ( $2\text{HCl} = \text{CO}_2$ )

(h) Potassium, bromine and iodine. The qualitative tests for these three bodies can be carried out in the following manner:

A large quantity of the brine is evaporated to  $\frac{1}{3}$  its original volume. Any salt which separates is filtered off or thoroughly drained. The filtrate is again evaporated, and any salt which separates is removed as before. The mother-liquor is then divided into two portions. In the one, by means of platinic chloride, a test is made for potassium, which is precipitated in form of yellow crystalline potassium-platinic chloride. To the other solution, which must be frequently agitated, chloroform and chlorine-water, drop by drop, are added. Iodine will first be precipitated—a fact readily noticed by the violet color of the chloroform. Later, bromine is recognized by the lemon or yellow color imparted to the chloroform layer.

The quantitative estimation of these three bodies will not be described here.

The results found are arranged according to the same principles which will be considered later under the determination of the more exact composition of boiler-water.

### 7. Crude Hydrochloric Acid.

This substance may contain as impurities: sulphuric acid, sulphurous acid, chlorine, arsenic and iron compounds, alumina, lime, alkali metals, hydrobromic acid and hydriodic acid.

The chlorine is usually to be attributed to the presence of nitrous acid in the sulphuric acid. Arsenic and iron compounds arise from the crude sulphuric acid. Qualitative tests for these various impurities are made by the usual method. (See also Sulphuric Acid.)

For the qualitative estimation of arsenic Krauch recommends the following procedure: To 1.0 gr. hydrochloric acid, diluted with 10

c.c. water, 5 c.c. freshly-prepared hydrogen sulphide water are carefully added, so as to form a supernatant layer. In the absence of arsenic no coloration and no yellow ring should form between the two liquids when warm or cold.

Of the quantitative determinations particular attention is called to those of arsenic, iron and sulphurous acid.

(a) Arsenic. In order to reduce any arsenic acid present, sulphurous acid is conducted into the solution for a protracted period. The latter, after expulsion of the sulphurous acid, is saturated with hydrogen sulphide, when arsenic is precipitated as trisulphide. The precipitate is filtered, thoroughly washed, dissolved from the filter with ammonia, and evaporated in a weighed glass or porcelain dish, after which the trisulphide remaining is dried at  $100^{\circ}$  and weighed.

(b) Iron. A measured quantity of the acid is treated with zinc, free from iron, in a current of carbonic acid, in order to reduce all the iron present. To the copiously diluted acid a 20 per cent. solution of manganous chloride or sulphate is then added, and the liquid is titrated with an accurately standardized, about  $\frac{1}{20}$  normal, potassium permanganate solution.

(c) Sulphurous acid. This is oxidized with permanganate, iodine or hydrogen peroxide to sulphuric acid, and precipitated with barium chloride. Sulphuric acid originally present must likewise be estimated and subtracted from the above.

### 8. Soda.

At present soda is derived principally from two well-known processes—the Le Blanc and the ammonia soda process. That from the former may contain, as chief impurities: sodium sulphate, sodium chloride, sodium silicate, sodium aluminate, sodium hydrate, sodium sulphide, sodium sulphite, ferric oxide, calcium carbonate, silica and carbon. Ammonia soda is mostly very pure, and contains as a rule only sodium chloride ( $\frac{1}{2}$  to about  $2\frac{1}{2}$  per cent.), at times sodium bicarbonate, and at the most only traces of sodium hydrate. At the same time it must be admitted that at present the Le Blanc soda comes into commerce in a very pure state on account of the general demand for soda containing not more than 0.4 per cent. matter insoluble in water, 0.1 per cent. matter insoluble in hydrochloric acid, and about 0.02 per cent. ferric oxide.

Following are the methods of investigation for technical soda selected with regard to its possible impurities. It is hardly necessary to state that the simultaneous presence of many of the impurities cited, such as hydrate and bicarbonate of soda, for instance, is excluded. It is an advantage to find out qualitatively the presence of individual constituents such as sodium hydrate, sodium sulphide, and sodium sulphite.

The qualitative examination for sodium hydrate is similar to the quantitative. The soda solution is precipitated with an excess of barium chloride, and the filtrate is tested for alkali by means of litmus or phenol-phthalein. The presence of sulphide of soda is determined by means of an alkaline solution of sodium nitroprusside or lead-paper. To test for sodium sulphite a sample is acidified with acetic acid, starch paste is added, and notice is taken whether a slowly-added dilute iodine solution is decolorized.

#### Quantitative Examination.

53 grs. soda (corresponding to one-half the molecular weight) are first dissolved in warm water in a large beaker glass, allowed to stand for  $\frac{1}{2}$  hour, and then filtered through a dried and weighed filter into a liter flask. After washing the filter the flask is filled to the mark. The residue is dried at  $100^{\circ}$  to constant weight, which represents the matter "insoluble in water." Should a more thorough examination of this be necessary, the filter is again moistened with water and lixiviated with hot dilute hydrochloric acid. Ferric oxide, alumina, calcium carbonate and magnesium carbonate are dissolved. If the filter now be washed, dried and weighed, it will contain the silica and carbon. By ignition of the filter the carbon is burned off, and the ash which is weighed consists only of silica. In the acid filtrate iron only is usually quantitatively estimated. To accomplish this ammonia is added, and the resulting ferric hydrate is dissolved in 1 : 4 sulphuric acid, reduced with zinc and titrated with permanganate. The remainder of the insoluble matter, after deducting ferric oxide, silica and carbon, may be considered as calcium carbonate.

#### Examination of the Aqueous Solution.

(a) Total active soda (with acid). 50 c.c. solution, representing 2.65 grs. soda, are titrated with hydrochloric acid (preferably  $\frac{1}{2}$

normal), with addition of methyl-orange, and the result is calculated as sodium carbonate. This includes as sodium carbonate sodium hydrate, sodium sulphide, sodium sulphite, sodium silicate, sodium aluminate, and finally sodium bicarbonate.

(b) Sodium sulphate. 50-100 c.c. solution are acidified slightly with hydrochloric acid, and the hot solution is precipitated with barium chloride.

(c) Sodium chloride. 20-50 c.c. solution are acidified with nitric acid and precipitated with silver nitrate. The presence of considerable quantities of sodium sulphide will influence the accuracy.

(d) Sodium hydrate. 100 c.c. soda solution are mixed in a large beaker with a few drops of phenol-phthalein and 150 c.c. of a 10 per cent. barium chloride solution. The solution is copiously diluted and titrated with  $\frac{1}{10}$ th normal oxalic acid. Previous filtration is unnecessary.

(e) Sodium sulphide. 100 c.c. solution are brought to boiling, and after the addition of ammonia an ammoniacal silver solution is added drop by drop until no further precipitation of silver sulphide ensues. In order to aid this observation the solution is filtered near the end of the operation, and the filtrate is titrated further. This is repeated until only a slight turbidity appears in the filtrate. To prepare the ammoniacal silver solution 13.845 grs. pure silver are dissolved in pure nitric acid, 250 c.c. ammonia are added to the solution, and the whole is diluted to one liter. Every c.c. of this solution represents 0.005 gr.  $\text{Na}_2\text{S}$ .

(f) Sodium sulphite. 100 c.c. soda solution are acidified with acetic acid, starch paste is added, and the solution is titrated with  $\frac{1}{10}$ th normal iodine solution until the blue coloration appears. 2 atoms iodine represent 1 molecule sodium sulphite, or 1 c.c. iodine solution = 0.0063 gr.  $\text{Na}_2\text{SO}_3$ . The sodium sulphide found in (e) calculated into sodium sulphite must be subtracted from this result.

(g) Sodium silicate and sodium aluminate. 100 c.c. solution are acidified in a spacious porcelain dish with hydrochloric acid and evaporated to dryness. The silica is separated as usual, and in the filtrate the alumina is determined by precipitation with ammonia.

(h) Bicarbonate. The estimation depends on the fact that

bicarbonate is changed to normal carbonate by the addition of caustic soda. If, therefore, an excess of titrated caustic soda be added to the soda solution, the carbonate be precipitated with barium chloride, and the excess of sodium hydrate be titrated, then the amount of hydrate used represents the quantity of bicarbonate present; in fact, 1 molecule sodium hydrate is equivalent to 1 molecule bicarbonate according to the equation



To conduct this, a separate portion of the soda (about 5 grs.) is weighed and dissolved in a beaker of about 1 liter capacity, with 100 c.c. water which has been previously boiled and cooled to 15–20°. Agitation and warming the solution are to be avoided, since the bicarbonate will lose carbonic acid thereby; on the other hand, by crushing the soda in the vessel solution may be accelerated. 25 c.c.  $\frac{1}{2}$  normal sodium hydrate solution are now added, followed by 150 c.c. 10 per cent. barium chloride and a few drops of phenol-phthalein. About 500 c.c. distilled water are added, and the excess of alkali is titrated with  $\frac{1}{2}$  normal oxalic acid.

Since sodium hydrate usually contains carbonate, 25 c.c. are simultaneously diluted with 100 c.c. water, 150 c.c. barium chloride, and a few drops of phenol phthalein are added, and the solution titrated with  $\frac{1}{2}$  normal oxalic acid. Should 24.75 c.c. oxalic acid (instead of 25) be required, they will represent the actual amount of caustic soda in the solution.

*Calculation.*—If 5 grs. soda were taken, and in titrating 13.5 c.c.  $\frac{1}{2}$  normal oxalic acid were used, then  $24.75 - 13.5 = 11.25$  c.c.  $\frac{1}{2}$  normal oxalic acid, required by the bicarbonate. These correspond to  $0.02 \times 11.25 = 0.225$  gr. caustic soda. According to the proportion  $40(\text{NaOH}) : 84(\text{NaHCO}_3) = 0.225 : x$ ,  $x = 0.4725$  gr.  $\text{NaHCO}_3$  or 9.45 per cent. bicarbonate.

(i) Moisture. This important determination is conducted by heating about 2 grs. soda in a platinum crucible at a low heat, and determining the consequent loss in weight. Any bicarbonate present is thereby decomposed. In the same manner silica will expel an equivalent quantity of carbonic acid. On account of the comparatively small error produced, simple desiccation over concentrated sulphuric acid is also recommended.

Freshly-prepared soda should not contain more than  $\frac{1}{4}$ - $\frac{1}{2}$  per cent. moisture. Even well-preserved soda, after some time, should not contain much over 1 per cent. Stored in moist air, however, the quantity of moisture can rise to 10 per cent.

#### Arrangement of the Analytical Results.

When the insoluble constituents are determined only to the extent mentioned, the calculation is very simple. The amounts of soda corresponding to caustic soda, sodium sulphide, sodium sulphite, sodium bicarbonate—furthermore, sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and sodium aluminate ( $\text{Na}_2\text{Al}_2\text{O}_4$ )—are calculated into sodium carbonate, and the sum of these is subtracted from the results obtained under (a). In this manner the true amount of sodium carbonate is obtained. This could also be done by a direct estimation of the carbonic acid and subsequent calculation into carbonate of soda—a process often preferred. The strength of a soda is expressed in degrees. German degrees represent the strength expressed as carbonate of soda; French, or Gay-Lussac, as oxide of sodium. Descroizilles degrees show how many parts by weight of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) are neutralized by 100 parts soda. These degrees bear the following relation to one another: 53.04 German degrees equal 31.04 Gay-Lussac or 49 Descroizilles degrees.

#### 9. Sodium Aluminate.

This contains, besides its two constituents, small quantities of matter insoluble in water, silica and traces of iron, which are determined in the usual manner.

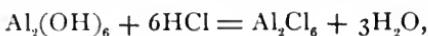
The estimation of soda and alumina is carried out volumetrically by the method of Lunge. The method is based on the following process: If to a solution of sodium aluminate hydrochloric acid be added, the soda is neutralized and alumina begins to separate. This is explained by the following reaction:



Were phenol-phthalein present, the color would disappear as soon as the soda was neutralized. The quantity of acid used, therefore, is a measure for the amount of soda present; in fact, 2 molecules hydrochloric acid correspond to 1 molecule sodium oxide, or when

$\frac{1}{2}$  normal hydrochloric acid is used, 1 c.c. of the latter corresponds to 0.0155 gr.,  $\text{Na}_2\text{O}$ .

If the addition of hydrochloric acid be continued in the presence of methyl-orange as indicator, a permanent red coloration sets in only when all the alumina has redissolved. Hence, according to the formula,



6 molecules hydrochloric acid are used for every molecule of alumina. 1 c.c.  $\frac{1}{2}$  normal hydrochloric acid, therefore, corresponds to 0.0085 gr. alumina.

To accomplish this about 0.5 gr. sodium aluminate is dissolved in hot water and titrated to decolorization with  $\frac{1}{2}$  normal hydrochloric acid, using phenol-phthalein as indicator. The acid used is recorded, 1-2 drops methyl-orange are added, and the solution is titrated with the same acid until it assumes a permanent red color. The calculation of the amount of sodium oxide and alumina is explained by the above statements.

## 10. Weldon Mud.

The investigation of the starting-products for the manufacture of chlorine, pyrolusite, as well as bleaching-lime, is supposed to be known. On the other hand, the examination of Weldon mud according to the procedure of Lunge will be described more fully. In this the amount of manganese dioxide, the total manganese and the "basis" are determined.

(a) Manganese dioxide. An acid ferrous iron solution, containing 100 grs. crystallized ferrous sulphate (or the equivalent amount of ferrous double salt), and 100 c.c. pure concentrated sulphuric acid to the liter, is accurately titrated with one-half normal permanganate solution. Thereupon, 25 c.c. iron solution are measured off into a beaker by means of a glass pipette. Ten c.c. of the well-agitated mud are drawn into a pipette, the latter is washed externally, the contents are placed with the iron solution in the beaker, and the adhering mud is washed out into the latter. When all has dissolved, on agitation, about 100 c.c. water are added, and the solution is then titrated with the permanganate solution. Let the amount of the latter solution = y, the amount of permanganate

used in titrating 25 c.c. iron solution =  $x$ ; then the amount of manganese dioxide per liter is found to be :

$$2.175 (x-y).$$

(b) Total manganese. Ten c.c. mud, drawn off as in (a), are boiled with conc. hydrochloric acid until chlorine has disappeared. Precipitated chalk is then added to neutralize the excess of acid. A conc. filtered bleaching-lime solution is added, and the mass is boiled for several minutes, after which the red color which appears is removed by the careful addition of alcohol. All the manganese is precipitated as dioxide.\* This is filtered off and washed until the filtrate no longer reacts with potassium iodide-starch paper. The precipitate, on the filter, is added to 25 c.c. of the acid iron solution, and if all the dioxide refuses to dissolve, an additional 25 c.c. are added. One hundred c.c. water are added, followed by titration with permanganate. The calculation carried out as under (a) gives the total manganese in the form of dioxide.

(c) Basis. By this term is understood the monoxides, etc., contained in the mud, which react with hydrochloric acid, but do not generate chlorine.

Twenty-five c.c. (with very high basis, 50 c.c.) normal oxalic acid solution are diluted to about 100 c.c. and heated to 60-80° C. 10 c.c. manganese mud are added with the above precautions, and the solution is shaken until the precipitate is a pure white, with no yellow tinge, a change which takes place rapidly at the above temperature. The solution is diluted to 202 c.c. (2 c.c. correspond to the volume of precipitate, and are marked on a 200 c.c. flask) and 100 c.c. of the filtrate are titrated back with sodium hydrate, using phenol phthalein as indicator. The number of c.c. sodium hydrate solution used =  $z$ , and therefore for the original solution =  $2z$ .

The oxalic acid (1) decomposes the manganese dioxide, yielding manganous oxide and carbonic acid; (2) binds the manganous oxide liberated; (3) saturates the monoxides, including manganese oxide originally present; (4) forms an excess =  $2z$ . The quantities of oxalic acid used in 1 and 2 are the same, and together equal

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\* When completely precipitated, the filtrate will not turn brown on adding bleaching-lime solution.

the value  $x-y$  in (a), since the oxalic acid is normal, but the permanganate only half normal. The value  $z$  represents the original amount of oxalic acid used, less the quantity  $(x-y)$  used in 1 and 2, and the excess  $zz$ . It is therefore equal to:  $25-x + y-2z$  respectively  $50-x + y-2z$ .

By "basis" is understood the relation of the value of  $z$  to  $a$ , the latter expressed by  $\frac{x-y}{2}$  (since the alkali is normal and the permanganate one-half normal).

When 25 c.c. oxalic acid are used, therefore, it =

$$\frac{25-x+y-2z}{x-y} = \frac{50-2x+2y-4z}{x-y} = \frac{50-4z}{x-y} - 2$$

and when 50 c.c. oxalic acid are used  $\frac{100-4z}{x-y}-2$ .

### Boiler-Water.

The complete analysis of a water used for technical purposes embraces the following determinations: Total solids, silica, ferric oxide, alumina, lime, magnesia, alkali, chlorine, sulphuric acid, carbonic acid and nitric acid. In addition to these, nitrous acid and ammonia may be qualitatively tested for. If necessary the water is filtered through a dry filter before the analysis.

(a) Total solids. 500-1000 c.c. water are evaporated in a weighed platinum dish and the residue is dried at 160-180°, to approximately constant weight. It may be remarked, however, that on account of the ready decomposition of magnesium salts, particularly magnesium chloride, on the one hand, and the difficulty encountered in completely expelling all the water of crystallization from gypsum and calcium chloride, on the other hand, the results are never concordant.

(b) Silica, ferric oxide, alumina, lime, and magnesia.

One liter (sometimes more) water is evaporated, with hydrochloric acid, in a porcelain dish; the silica is separated, ammonium chloride is added, and the iron and alumina are precipitated with ammonia.

In presence of a large quantity of magnesia the precipitate is dissolved, re-precipitated, and both constituents are ignited and weighed together.

In the filtrate the lime is precipitated with ammonium oxalate.

The precipitate is then carefully heated in a porcelain crucible until the evolution of carbonic acid ceases, and is then ignited over a blast-lamp to constant weight, and weighed as calcium oxide. The magnesia is then precipitated in the filtrate with sodium hydrogen phosphate in the usual manner.

(c) Alkalies. These are determined indirectly in the total solids by weighing the sulphate residue. For this purpose the solids are ignited at a low heat in the platinum dish, and then dissolved in dilute hydrochloric acid under cover of a watch-glass. The mass is finally evaporated with 10-12 drops concentrated sulphuric acid, and after expelling the acid it is ignited and weighed.

If then the sum of the lime and magnesia, previously determined and calculated into sulphates, plus the quantities of silica, ferric oxide and alumina found, be subtracted from the sulphate residue, there remain the alkali sulphates present, which are considered as sodium sulphate and are calculated into sodium oxide.

(d) Chlorine. Depending on the result of a qualitative test,  $\frac{1}{4}$ -1 liter water, after concentration, is acidified with nitric acid and precipitated in the usual manner with silver nitrate.

(e) Sulphuric acid.  $\frac{1}{4}$ -1 liter water, acidified with hydrochloric acid, and, if necessary, concentrated, is precipitated with barium chloride in the usual manner.

(f) Carbonic acid. The combined carbonic acid present is estimated in  $\frac{1}{2}$ -1 liter by adding methyl-orange and titrating to red coloration with  $\frac{1}{10}$  normal hydrochloric acid. The calculation is made as normal carbonate; hence  $2\text{HCl} = \text{CO}_2$ . The estimation of free carbonic acid in a technical analysis may be omitted.

(g) Nitric acid. The qualitative test is best made with the diphenylamine reaction. (See Sulphuric Acid.) For quantitative estimation the method of Schulze-Tiemann is best employed. In this, by means of ferrous chloride and hydrochloric acid, the nitric acid is reduced to nitric oxide, and the latter is determined volumetrically. The details are too well known to describe.\*

The qualitative test for nitrous acid, of which only minute quantities are present, is best made by the reaction of Griess. A small quantity of sulphanilic acid solution (5 grs. in 150 c.c. dilute acetic

\* See also Fresenius, Quantitative Analysis, Vol. II., p. 155.

acid) is added to a small quantity of the water in a test-tube and warmed to 80°, when a solution of  $\alpha$ -naphthylamine (.05 gr. in 150 c.c. dilute acetic acid) is added. In the presence of nitrous acid a red coloration ensues either immediately or after a few minutes.

To test for ammonia qualitatively about 5 c.c. Nessler's reagent\* are added to 100 c.c. water, and the change noticed from above down through the liquid. Ammonia causes a yellow coloration. When the water is very hard or chalybeate, it is better to precipitate first with pure caustic soda and subsequently examine the filtrate.

*Arrangement of results.*—Chlorine is bound to sodium and any remainder to calcium. Sulphuric acid is bound to lime, nitric acid to ammonia, any residue to sodium, providing the chlorine has not fully used up the latter, otherwise to magnesia. The remaining lime and magnesia are bound to carbonic acid in the form of carbonates.

Silica is expressed as such.

#### Shorter Procedure.

It is often desirable to circumvent the execution of a complete analysis by the use of a shortened procedure, which allows a more or less complete insight into the composition of a water.

As such the method of Kalmann and the direct determination of hardness according to Clark are described.

The method of Kalmann limits itself to the following determinations :

(a) Combined carbonic acid. This is ascertained by the process described under (f) in the complete analysis.

(b) Lime. This is determined by the direct precipitation of a measured volume of water by means of ammonium oxalate. The separation of the silica, ferric oxide and alumina is not necessary.

(c) Magnesia is determined in the filtrate from (b) by the usual precipitation with sodium hydrogen phosphate.

The various results are reckoned on 1 liter water. On the basis

\* To prepare this, 50 grs. potassium iodide are dissolved in 50 c.c. hot water and to it is added a hot concentrated mercuric chloride solution until the precipitate of mercuric iodide formed no longer dissolves. The solution is filtered, 150 grs. caustic potash in concentrated solution are added, and the whole is diluted to one liter. An additional 5 c.c. mercuric chloride solution are added, the solution is allowed to settle, and the clear supernatant liquid is poured off.

of these results the preparation of water for technical uses can be made. This will subsequently be described more fully.

*Estimation of hardness according to Clark.*—The hardness of a water depends on the amount of calcium and magnesium salts present. It is divided into temporary hardness, due to bicarbonates of calcium and magnesium, which disappears in consequence of the precipitation of the insoluble monocarbonate when the water is boiled, and permanent hardness, which is due to any remaining calcium and magnesium salts. Temporary and permanent hardness represent the total hardness of water.

The hardness of water is expressed in degrees which are distinguished as German, French and English degrees of hardness. The German degrees represent the number of milligrammes calcium oxide in 100 c.c. water. Any magnesium oxide is hereby reckoned in the form of the equivalent amount of calcium oxide. French degrees state the equivalent amount of calcium carbonate, whereas English degrees of hardness express the number of milligrammes calcium carbonate contained in 70 parts water. German, French and English degrees of hardness stand in the ratio of .56 : 1 : .70. As a rule, the result is expressed in German degrees.

The method of Clark depends on the fact that soap solutions precipitate all calcium and magnesium salts in the form of insoluble soaps. A slight excess of soap is recognized by the permanent lather formed on the liquid on shaking.

*Preparation of the normal soap solution.*—10 grs. finely-shaved Marseilles soap are dissolved in 1 liter 95 per cent. alcohol. The solution is filtered, and to every 200 grs. solution a mixture of 150 c.c. water and 130 grs. alcohol, above strength, is added. The solution so obtained is now standardized in such a manner that 45 c.c. correspond to 12 degrees hardness. To accomplish this a solution of normal hardness is prepared which contains 12 mg. calcium oxide in 100 c.c. or an equivalent quantity of barium oxide. Such can be made by dissolving .3686 gr. selenite ( $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ) or .523 gr. pure crystallized barium chloride in 1 liter distilled water. To 100 c.c. of this hard water in a glass-stoppered flask of about 200 c.c. capacity, the soap solution is added from a burette until a thick froth lasting five minutes just forms on the surface on shaking. Should less than 45 c.c. of the soap solution be used, as

is usually the case, then from the result obtained in the titration the dilution of the alcohol and water soap mixture, necessary to bring the solution to the required strength, is calculated. After the proper dilution a second titration is made. Should this not yield the desired result, the above process is repeated.

*Determination of the hardness.*—For every determination 100 c.c. of the water must be used. However, since the soap solution is suitable only for waters possessing a hardness up to 12°, and since also the end reaction is more easily recognized in waters moderately hard, it is advisable to use only 50 c.c. of a very hard water and dilute the same with distilled water to 100 c.c. The water is placed in a stoppered flask as before, the soap solution is then added from a burette, and the liquid is shaken. In the place of the above-mentioned end reaction, Kalmann calls attention to the nature of the lather and the perceptible sound produced on shaking. The lather should remain firm, that is, the bubbles should not break immediately after shaking. The sound becomes dull and is not as clear as that produced by water enclosed in glass.

It often happens that after binding the lime with the fatty acids of the soap, the froth becomes firm and the sound becomes muffled. The reading is made at this point, and more soap solution is added. No further change should take place if the end reaction has been reached. When the hardness due to magnesia is not yet neutralized, the bubbles will again become frail and the sound clear. In this case the titration is carried further until the end reaction is reached. The phenomenon is so characteristic that at times it permits of an approximately quantitative estimation of lime and magnesia.

Since the relation is not constant between soap solution used and hardness, use must be made of the following table. The hardness found is to be estimated on 100 c.c. of the original water.

The method of Clark gives the total hardness. Should it be necessary to determine also the temporary hardness,  $\frac{1}{2}$ —1 liter water is titrated with  $\frac{1}{10}$  normal hydrochloric acid, using methyl-orange as indicator, and the amount of acid used is computed as lime. The amount of lime in 100 c.c. represents the total hardness. The permanent hardness is gotten by difference.

Table of German Degrees.\*

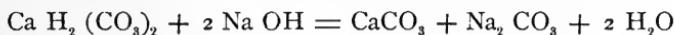
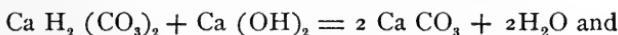
c.c. Soap- solution.	Hard- ness.								
1.8	0.1	11.3	2.5	20.4	4.9	29.1	7.3	37.4	9.7
2.2	0.2	11.7	2.6	20.8	5.0	29.5	7.4	37.8	9.8
2.6	0.3	12.1	2.7	21.2	5.1	29.8	7.5	38.1	9.9
3.0	0.4	12.4	2.8	21.6	5.2	30.2	7.6	38.4	10.0
3.4	0.5	12.8	2.9	21.9	5.3	30.6	7.7	38.8	10.1
3.8	0.6	13.2	3.0	22.3	5.4	30.9	7.8	39.1	10.2
4.2	0.7	13.6	3.1	22.6	5.5	31.3	7.9	39.5	10.3
4.6	0.8	14.0	3.2	23.0	5.6	31.6	8.0	39.8	10.4
5.0	0.9	14.3	3.3	23.3	5.7	32.0	8.1	40.1	10.5
5.4	1.0	14.7	3.4	23.7	5.8	32.3	8.2	40.5	10.6
5.8	1.1	15.1	3.5	24.0	5.9	32.7	8.3	40.8	10.7
6.2	1.2	15.5	3.6	24.4	6.0	33.0	8.4	41.2	10.8
6.6	1.3	15.9	3.7	24.8	6.1	33.3	8.5	41.5	10.9
7.0	1.4	16.2	3.8	25.1	6.2	33.7	8.6	41.8	11.0
7.4	1.5	16.6	3.9	25.5	6.3	34.0	8.7	42.2	11.1
7.8	1.6	17.0	4.0	25.8	6.4	34.4	8.8	42.5	11.2
8.2	1.7	17.4	4.1	26.2	6.5	34.7	8.9	42.8	11.3
8.6	1.8	17.7	4.2	26.6	6.6	35.0	9.0	43.1	11.4
9.0	1.9	18.1	4.3	26.9	6.7	35.4	9.1	43.4	11.5
9.4	2.0	18.5	4.4	27.3	6.8	35.7	9.2	43.8	11.6
9.8	2.1	18.9	4.5	27.6	6.9	36.1	9.3	44.1	11.7
10.2	2.2	19.3	4.6	28.0	7.0	36.4	9.4	44.4	11.8
10.6	2.3	19.7	4.7	28.4	7.1	36.7	9.5	44.7	11.9
11.0	2.4	20.0	4.8	28.8	7.2	37.1	9.6	45.0	12.0

## Preparation of Water for Technical Purposes.

In this the precipitation of constituents of the water which cause hardness is aimed at. Of the different methods proposed for the purpose, only the very useful method of Stingl and Bérenger will be more fully described.

According to this procedure there are precipitated :

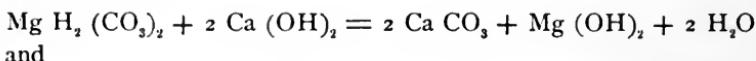
1. The bicarbonate of calcium present in the water, by means of calcium hydrate or sodium hydrate. For every molecule calcium bicarbonate, 1 molecule calcium hydrate or 2 molecules sodium hydrate are necessary, according to the equations :



2. The bicarbonate of magnesium by the same precipitants, of

\* Taken from Kalmann's Kurzer Anleitung zur chem. Untersuchung, etc.

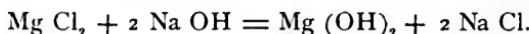
which double the quantities must be taken on account of the solubility of normal magnesium carbonate, which is thereby precipitated as hydrate.



3. All the remaining calcium salts with sodium carbonate, of which 1 molecule is necessary for every molecule lime.



4. All remaining magnesium salts with caustic soda. For every molecule MgO, 2 molecules Na OH are needed.



Evidently, it follows from 1 and 2 that when sodium hydrate is used for precipitation, an equivalent amount of sodium carbonate is formed in solution, which at times may precipitate the whole of the lime salts present. From this, given the precipitants mentioned, the three following conditions may be deduced :

(a) *The quantity of soda is greater than that required by (3) to precipitate the calcium salt.* In this instance, in order to avoid the formation of an excess of sodium carbonate, an equivalent part of the sodium hydrate is replaced by calcium hydrate. Therefore, the preparation requires *sodium hydrate and calcium hydrate*.

(b) *The soda formed is less than the amount required for the precipitation of all remaining lime salts.* The purification is then conducted with use of caustic soda and soda.

(c) *The soda formed is equal to the amount required for the precipitation of calcium salts.* In this instance only caustic soda is necessary for purification.

In all three instances the quantity of caustic soda required to precipitate any magnesia not present as bicarbonate (4) is added.

*Calculation.*—The values from the shortened procedure of Kalmann, or the complete analysis for bound carbonic acid, total lime and total magnesia, are calculated into equivalents of lime. The results so obtained will be :

for bound carbonic acid	$\alpha$ g	Ca O
for total lime	$\beta$ g	Ca O
for total magnesia and total lime (total hardness)	$\gamma$ g	Ca O

The difference  $2\alpha - \beta$  is now found. Should this be positive, there is present the condition described under ( $\alpha$ ). For purification there are used:  $(2\alpha - \beta)$  parts by weight lime (dissolved in 800 times the quantity of water), and an amount of caustic soda equivalent to  $(\gamma - \alpha)$  parts by weight lime. Instead of using prepared caustic soda, the latter can be produced from slaked lime and soda. For this purpose  $(\gamma - \alpha)$  parts by weight lime and the equivalent quantity of soda are used.

Should the difference  $2\alpha - \beta$  prove to be negative, condition  $\beta$  exists.

For purification there is used the quantity of soda equivalent to the difference of  $(\gamma - \alpha)$  g. lime, and  $(\gamma + \alpha - \beta)$  g. lime, which renders a part of the soda caustic.

Finally, should the difference  $2\alpha - \beta = 0$ , condition  $\alpha$  exists.

For purification, a quantity of caustic soda equivalent to  $(\gamma - \alpha)$  parts by weight lime, is necessary. This may be prepared by adding to  $(\gamma - \alpha)$  parts by weight lime, as in the case  $\alpha$ , an equivalent amount of soda.\*

## 12. Fuel.

The methods described are applicable to all kinds of fuel—anthracite, bituminous, lignite, etc.

As a rule, the determinations made in a coal analysis are water, ash, sulphur, and an elementary analysis. In addition to these, nitrogen and phosphorus, as well as the yield of coke, are frequently estimated.

(a) Water. The estimation of water in fuel.

The sample must be coarsely ground, about pea size, since during the process of pulverization considerable moisture is given off. Coal, especially anthracite coal, possesses the property of absorbing oxygen upon protracted drying, thereby causing an increase in

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\* The derivation of these methods of calculation of Kalmann may be found in the Mittheilung des K. K. technolg. Gewerbe Museum, 1890.

weight. It is best to heat about 20-50 grs. material in a weighing tube provided with a well-ground stopper, which is removed during the time of heating, and to weigh the same from hour to hour until no further loss occurs. Should perhaps the last weight show an increase, the previous result is accepted.

(b) Ash. The ignition is best carried out in a muffle, when, as a rule, one hour will be sufficient. Should a muffle not be accessible, about 1 gr. finely-divided coal is placed in a small platinum capsule and covered with the lid of a larger crucible. Heat is applied at first with a small flame to avoid sintering. Later the lid is removed, the capsule is tilted on the triangle, the lid is likewise brought into an inclined position on the capsule, and the latter is heated protractedly to a red heat with an ordinary-sized flame. When the ash appears uniform, which is usually the case after 2-3 hours, the capsule is weighed. The ash is now moistened with a few drops of alcohol, when any particles of carbon will rise to the surface, where they may be easily recognized. The alcohol is ignited and driven off, and the capsule is reweighed. This process is finally repeated a second time. Lunge advises the use of a platinum crucible, which is placed in the round opening of an inclined asbestos plate. Only the part of the crucible protruding beneath is heated. The air used for oxidation does not admix with the gases produced by the flame, and therefore acts more energetically.

(c) Sulphur. Sulphur is present in fuels in the form of sulphides (mostly pyrite), sulphates (calcium sulphate), and in combination with organic substances. The estimations usually made are: Total sulphur and sulphur present in form of metallic sulphides + sulphates. Sometimes a separate determination of sulphur due to sulphates is also made.

Total sulphur according to Eschka. About 1 gr. finely-divided coal is thoroughly mixed in a platinum crucible by means of a thick platinum rod, with 1.5-2 grs. of an intimate mixture of 2 parts pure ignited magnesia and 1 part anhydrous sodium carbonate. The crucible is inclined on the triangle, or in the perforated asbestos plate, without a lid, and the lower half only is brought to a red heat. Heat is applied for about 1 hour, with frequent stirring by means of the platinum rod. In that time the mass, at first gray, will have assumed a bright red or brown color. The contents are cov-

ered with hot water and rinsed into a beaker, the crucible is boiled out again, and bromine water is added until the liquid assumes a bright yellow color. This is done in order to oxidize any remaining sulphides. The solution is heated, filtered, and the filtrate is acidified with hydrochloric acid. It is then boiled in a draught-chamber until the deep brown colored liquid becomes colorless, and is then precipitated with barium chloride.

The magnesia-soda mixture had better be prepared in quantity. When sulphur is present in small quantity in this mixture, a considerable portion is used for a sulphur determination, and the corresponding quantity of the latter is subtracted from the total sulphur.

Sulphur present as sulphides and sulphates. According to Drown, a saturated solution of bromine in caustic soda, sp. gr. 1.25, to which sufficient caustic soda to absorb any free bromine has been added, is used to advantage for oxidation. About 1 gr. of the finely pulverized substance is moistened with 10 c.c. of this solution. It is then heated and acidified with hydrochloric acid. In the space of 10 minutes two quantities, 20 c.c. each, of the solution, are again added, and each time the solution is acidified with hydrochloric acid. After the last addition of acid, the mass is evaporated to dryness, dried at 110°–115° in an air-bath to convert silica into insoluble form, taken up with hydrochloric acid, filtered, and the filtrate is precipitated with barium chloride. The method is especially useful for anthracite coal.

*Sulphate sulphur.*—A considerable quantity of the sample is first incinerated, and a weighed quantity of the ash, 2–3 grs., is lixiviated with hot water. In order to oxidize any calcium sulphide formed, the solution is boiled with hydrogen peroxide or a few drops of bromine. It is then acidified with hydrochloric acid and precipitated with barium chloride.

(d) Elementary analysis. The execution of this is too well known to describe. It is, however, necessary to add special precautions pointed out by Böckmann, and also the authors.

While the estimation of hydrogen, as a rule, can be carried out with ease and accuracy, a difference in parallel determination of  $\frac{1}{2}$  to  $\frac{3}{4}$  per cent. is noticeable in determining the carbon, even when great care is exercised. The reason for this lies in the already mentioned tendency of carbon to sinter. In order to avoid this as

much as possible, it is advisable to conduct the first part of the combustion slowly. This can be accomplished by at first using a current of air (not immediately of oxygen) and by moderately heating the portion of the tube in proximity to the substance. It is also advisable not to have the substance too finely divided, thereby avoiding an immediate violent action. The finish of the preliminary step, which may be termed coking, is easily observed. The remaining operation is then carried out at a high heat in a current of oxygen, the flow of which through the wash-bottle is regulated to about 20 bubbles in every 10 seconds.

Charging the combustion tube is done in the usual manner. For many well-founded reasons it has been found decidedly advantageous to substitute for granular copper oxide a series of oxidized copper spirals. The addition of a silver or bright copper spiral is wholly unnecessary on account of the minute quantities of chlorine and nitrogen. On the other hand, an absorbent of the combustion-products of the sulphur is absolutely necessary. In the absence of such, sulphurous and sulphuric acid readily enter the absorption-bulbs, are absorbed, and increase the weight. It is only necessary, according to Fisher, to keep the oxide of copper in the front of the tube at a low red heat, whereby the oxide itself acts as a retainer of the combustion-products of sulphur. Nevertheless, it appears more advisable to fill the front part of the tube, which is allowed to protrude about 28 cm., with dry, coarsely-divided lead peroxide. The latter is placed in a tin case provided with a thermometer, and is heated to 180° during the combustion.

Further, be it noted that the dehydrated substance had best be used, and that a hydrogen determination be simultaneously conducted. The water thus found is deducted from the total water.

(e) Nitrogen. The method is found under the accurately described procedure of Kjeldahl in the chapter "Fertilizers." 0.8-1 gr. finely-divided coal is used in the determination.

(f) Phosphorus. This is always determined in the ash, and not the original substance. 1-2 grs. ash, obtained best by ignition in a muffle, are digested for a considerable length of time with hydrochloric acid in a porcelain dish, whereby, according to Muck, the phosphorus is quantitatively dissolved. The solution is evaporated to dryness, moistened with hydrochloric acid, and 100-150 c.c.

water are added. It is warmed on a water-bath, filtered into a second porcelain dish, and evaporated repeatedly almost to dryness with addition of nitric acid. The liquid is diluted with water acidified with nitric acid and precipitated in a beaker with molybdate solution.\* The remaining treatment is carried out in the well-known manner more fully described in the chapter on "Fertilizers."

(g) Coke. 1 gr. finely-divided coal is weighed in a smooth-walled platinum crucible, which it fills to the height of 30–35 mm., and the crucible is placed on a thin platinum triangle so as to bring its base 3 cm. from the mouth of a Bunsen burner. Strong heat is applied to the tightly-closed crucible from the beginning. The burner, which is provided with a protecting cone, should have a flame 18 cm. in height. Heat is applied until no luminous flame issues from between crucible and lid, an operation lasting 1½–2 minutes. The sooty film on the crucible-lid is also weighed. By following these directions accurately results may be obtained which agree within .2–.4 per cent.

*Arrangement of results.*—The results are as frequently based on air-dried as on dehydrated material. Oxygen is indirectly determined by deducting the sum of the water, carbon, hydrogen, sulphur,† nitrogen and ash found from 100. So called "disponible hydrogen" is that which remains upon deducting the quantity of hydrogen used to form "chemically-bound water" with the oxygen, e.g.,  $\frac{1}{8}$  of the oxygen, together with that present as hygroscopic water, from the total hydrogen.

*Absolute heating value.*—To calculate this, the formula lately recommended by Schwackhofer is employed,

$$E = \frac{8000C + 29,000H + 2500S - 600W}{100} \text{ calories,}$$

in which the symbols C, H, S, W represent the percentages of carbon, "disponible" hydrogen, sulphur and water (hygroscopic and chemically bound).

If the absolute heating value (E) be divided by 637, there results

\* Preparation, see under V, "Fertilizers."

† Excluding sulphur existing as sulphate.

the evaporative efficiency, that is, that weight of water at  $0^{\circ}$  which is changed to steam at  $100^{\circ}$  by one kilogram of coal.

### 13. Furnace Gases.

The investigation of gases of a furnace serves to regulate the feeding of the latter. Carbonic acid, oxygen, carbon monoxide and nitrogen, the latter by difference, are determined in furnace gases. For this purpose the apparatus of Orsat, whose arrangement is seen in the following illustration, Fig. 3, is best used :

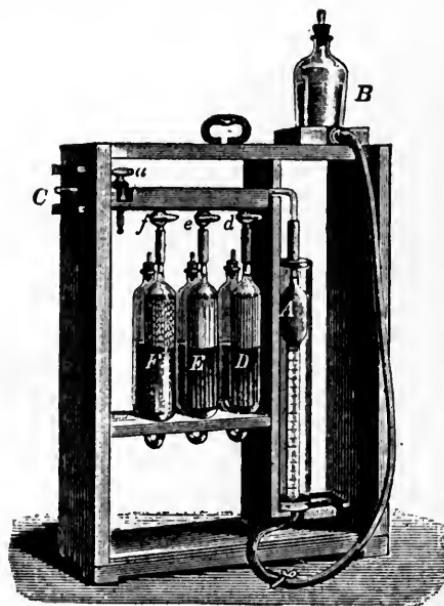


FIG. 3.—Orsat's Apparatus.

The gas burette *A* is bound to the leveling flask *B*, which is filled with water. By raising *B*, *A* is filled with water to the uppermost mark; by lowering *B* gas is drawn through the tube *C*, or from the absorption vessels *D*, *E*, *F*; by repeatedly raising *B*, simultaneously opening the stopcocks of *D*, *E* or *F*, the gas may be led into any of the latter. To establish the necessary communications the cocks *D*, *E*, *F*, and the three-way cock *A* are provided. In order to increase absorption the vessels *D*, *E* and *F* are provided with a large

number of narrow glass tubes. *D* is used to absorb carbonic acid, and is filled with 110 c.c. caustic potash solution (sp. gr. 1.20-1.8). *E* serves to absorb oxygen, and contains pyrogallic acid or thin phosphorus sticks immersed in water. In the latter case black paper surrounds the vessel to protect the contents from the action of light. Finally, for the absorption of carbon monoxide, the vessel *F* is filled with cuprous chloride solution prepared by shaking 200 grs. commercial cuprous chloride with a solution of 250 grs. ammonium chloride in 750 c.c. water in a stoppered flask, into which there is placed, later, a copper spiral which reaches to the bottom. Before using, 1 vol. ammonia (sp. gr. 0.905) is added to 3 vols. of this solution. Complete absorption takes place only upon prolonged contact; and, furthermore, the reagent must be frequently renewed. The absorption reagents are kept in the rear tubes, and are brought into those in front only when the apparatus is in use. This is accomplished by establishing communication with the outside air by means of stopcock *a*, closing *d*, *e* and *f*, filling *A* with water by raising *B*, arranging *a* to close off *A*, lowering *B* and opening the stopcock *d*. The liquid is thereby drawn from the rear into *D*. In a similar manner *E* and *F* are filled. The tube *c*, previously provided with a *U* tube, enclosing raw cotton to exclude dust, is now connected with the chamber from which the gas is to be taken, and by closing *d*, *e* and *f* and lowering *B*, a volume of gas sufficient to fill to the zero point is drawn.\*

The cock *d* is opened, *B* is raised, and the gas in the burette is forced into *D*. As soon as the water reaches the end division the flask is lowered, and the process is quickly repeated in order to bring the gas into thorough contact with the reagents. Finally the water-levels in flask and burette are brought to the same height, the stopcock *d* is closed, and the volume is read. The decrease in volume gives per cent. by volume of carbonic acid, since the burette is divided into 100 c.c. In the same manner the oxygen is subsequently determined by absorption in *E*, the carbon monoxide in *F*, and the nitrogen as remainder of 100.

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\* To completely remove air contained in the tubes, the gas forced in by lowering *B* is passed out through exit in *a*, fresh gas is drawn in, and the process is repeated.

For gases rich in hydrogen, such as water-gas, the apparatus of Orsat-Lunge is used. The latter is quite similar to the Orsat apparatus. The gas, freed from carbonic acid, oxygen and carbon monoxide, is mixed with a measured quantity of air, and is conducted through a capillary containing platinum asbestos or palladium asbestos. By heating the latter the hydrogen is burned. The residue is again measured in the burette, and  $\frac{2}{3}$  the decrease in volume is reckoned as hydrogen. (2 vols. hydrogen unite with 1 vol. oxygen.)

## II. Cement and Clay.

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THE raw materials for the products of this group are limestone, marl and clay.

### 1. Lime.

(a) Moisture. 3-5 grs. sample are heated to constant weight in a drying oven at  $110^{\circ}$ - $120^{\circ}$ .

(b) Silica and clay, ferric oxide, alumina, lime and magnesia. About 1 gr. powdered sample is uniformly moistened with water in a porcelain dish, covered with a watch-glass, and decomposed by addition of moderately dilute hydrochloric acid. After the evolution of carbonic acid has ceased the mass is evaporated to dryness on a water-bath with constant stirring, completely dried by heating on an asbestos plate, and covered with sufficient concentrated hydrochloric acid to completely dissolve all soluble matter. After a half-hour hot water is added, the solution is filtered, the precipitate is washed and weighed as silica and clay. To the hot filtrate, which has been oxidized with bromine water, ammonia is added to slight excess, the solution is boiled for a few moments, and the precipitate formed is filtered off. To free it from any adhering lime, the solution in hydrochloric acid and precipitation with ammonia may be repeated. Ferric oxide and alumina are determined together. A separate iron determination, when necessary, is conducted in another portion. The filtrate, now about 200 c.c. in volume, is brought to incipient boiling, the flame is removed, and ammonium oxalate is added to the point of complete precipitation and rapid deposition. A sufficient excess of ammonium oxalate is yet added to convert all magnesia into soluble magnesium oxalate. Finally the solution is diluted to 400-500 c.c. and allowed to stand several hours in a warm place. Frequently magnesia is thrown down together with the lime, but by gradual addition of the ammonium oxalate the magnesia can be reduced to about .02 per cent. If exact results be required, the precipitation may be repeated a second time.

For this purpose the clear liquid is decanted through a filter, the residue remaining in the beaker is stirred twice with hot water, and the clear liquid is decanted each time through the same filter. The precipitate in the beaker is redissolved in hydrochloric acid, and to the solution ammonia and ammonium oxalate are added in sufficient quantity. The reprecipitated calcium oxalate is allowed to stand one hour. The solution is then filtered through the same filter, the latter is washed thoroughly with hot water, dried, ignited for a time at a low heat, and is then ignited over a blast-lamp until constant weight is obtained. It is weighed as calcium oxide.\* The filtrate from the lime is made slightly acid with hydrochloric acid and is concentrated on a water-bath to about one-third its volume. One-third the remaining volume of dilute ammonia is added, and when cool the magnesia is precipitated with sodium hydrogen phosphate. After three hours the solution may be filtered. The precipitate is washed with water containing about 3 per cent. ammonia, then dried and ignited in a platinum crucible. The weight represents  $Mg_2P_2O_7$ .

(c) Oxide of iron and sulphuric acid.

Both constituents may when necessary be determined in the same operation. For this purpose about 10 grs. powdered sample are placed in a 250 c.c. flask, dissolved in hydrochloric acid, and diluted to the mark. Two hundred c.c. solution are filtered through a dry filter and precipitated with ammonia. The precipitate formed is dissolved in sulphuric acid (1 : 4), diluted with water, reduced with zinc and titrated with permanganate of potash. The filtrate from the sesquioxide of iron is acidified with hydrochloric acid, and the sulphuric acid is determined with barium chloride.

(d) Carbonic acid. Carbonic acid, as a rule, can be calculated by considering it bound to the calcium oxide and magnesia which remain after deducting that portion of the former attached to the sulphuric acid found. When large quantities of silica are present—in which case lime can exist as calcium silicate—a direct determination of carbonic acid is made in the usual manner by absorption in tubes containing soda lime.

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\* To check the result, it is advisable to titrate the calcium oxide with hydrochloric acid.

(e) Alkali metals are present only in traces, as a rule, and their estimation may be omitted.

(f) Organic matter. For an approximate result the method of Fresenius is useful. By this method the organic matter is determined by combustion in a current of oxygen. For every 58 parts carbon obtained (213 parts carbonic acid) 100 parts organic matter are allowed.

### Marl.

Limestones containing under 10 per cent. clay, *i.e.*, clay, silica and sesquioxides, yield "fat lime" on being calcined, and are suitable for the preparation of lime cements. Limestones containing over 10 per cent. of such constituents yield "lean lime." They are termed argillaceous limestones or marls. A further distinction is made between calcareous and clayey marls, depending on the predominance of one or the other constituent.

The analysis of marl is, as a rule, carried out in the manner of a limestone analysis, with the avoidance, nevertheless, of too great an excess of hydrochloric acid and excessive heating when dissolving. In addition, a determination of clay, insoluble in hydrochloric acid, is made. This applies mainly to the determination of soluble silica, coarse and fine sand.

(a) Soluble silica. The residue, insoluble in hydrochloric acid, obtained from 1-2 grs. sample, is removed from the filter and lixiviated by boiling several times with renewed portions of caustic soda or chemically pure soda in a porcelain or platinum dish until the filtrate fails to show silica as turbidity upon addition of ammonium chloride followed by boiling. The silica in the alkaline extractions of the residue is determined in the usual manner after precipitation with hydrochloric acid and evaporation to dryness.

(b) Coarse and fine sand. Hydrochloric acid is added to 50 grs. substance. The solution is boiled  $\frac{1}{2}$  hour, and the residue is subjected to the washing process described under "Clay."

The investigation of marl rich in clay may also be conducted by the method described under "Clay."

Marls which contain 20-30 per cent. clay are best suited, on the average, for the preparation of hydraulic cement. On the other hand, those marls, the clay in which contains an excessive amount of free silica, yield only ordinary hydraulic cements, particularly

when the latter is present, for the greater part, as common sand and not powdered sand. Briefly, the more the clay in a marl is present as silicates, not free silica, and the less coarse sand it contains, the better hydraulic cement will it yield. In addition, the requisite proportion of clay to lime must be present.

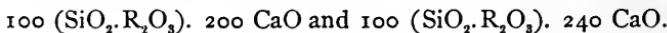
By mixing clay with limestone and calcining the mixture until sintered, products are obtained which, upon pulverizing, possess the properties of a hydraulic cement and are known as Portland cement. The limestone is used in form of chalk or marl, and should not contain too much magnesia. While magnesia to an extent of 3 per cent. operates advantageously, considerable quantities are harmful, and about 18 per cent. has a decidedly disadvantageous effect on the hardness of the cement.

The clay used is preferably one containing little sand (especially coarse sand), much silica, and a rather high amount of iron oxide and alkali. Such clays are usually easily fusible and show the following average composition :

	Per cent.
Silica, . . . . .	59-68
Alumina, . . . . .	12-23
Ferric oxide, . . . . .	7-14
Lime, . . . . .	75-10
Magnesia, . . . . .	1-3
Alkali, . . . . .	2-4

According to Michaelis, it is preferable that the proportion of clay to lime in the mixture be such that in the calcined Portland cement there be 210-230 equivalents of alkaline earths and 15-25 equivalents clay, plus ferric oxide, to 80 equivalents silicate.

If silica and sesquioxides (as acids) be reckoned on lime, then the following expression is obtained :



Under 200 CaO disintegration occurs; above 240 spreading occurs, and it is advantageous not to exceed 220.

Kosmann states that there should be present in the mixture

$$\begin{aligned} 6 \text{ Mol. CaO} &= 60.21 \text{ per cent.} \\ 2 \text{ " SiO}_2 &= 21.50 \text{ "} \\ 1 \text{ " Al}_2\text{O}_3 &= 18.29 \text{ "} \end{aligned}$$

But on account of the presence of a not inconsiderable quantity of free silica in the limestone and clay, the above proportion must practically be increased  $2\frac{1}{2}$ - $2\frac{5}{8}$   $\text{SiO}_2$  and decreased .5-.66  $\text{Al}_2\text{O}_3$ .

The extreme limits in the composition of Portland cements, according to Candlon, are :

	Per cent.
Lime,	58-67
Silica,	20-26
Alumina,	5-10
Magnesia,	.5- 3
Sulphuric Acid,	.5- 2

The chemical investigation of finished cements is conducted in exactly the same manner as that of limestone or marl. Frequently the mere determination of clay (total silicates) is required. For this purpose 2 grs. cement are covered in a capsule with 20 c.c. water and decomposed with hydrochloric acid, to which nitric acid has been added. Thereupon the solution is brought to boiling, precipitated with ammonia, and the precipitate formed is weighed. Good cement should dissolve almost completely in concentrated hydrochloric acid, since, in consequence of the treatment undergone, the silica is transformed into a soluble modification.

### 3. Clay.

In a broad sense clay is understood to be a hydrated aluminium silicate, which in addition to argillaceous matter can contain among other admixtures unaltered feldspar and silica, frequently also iron, lime, magnesia, alkalies, and minute quantities of manganous oxide, as well as volatile constituents.

Concerning the part played by the individual constituents, the following may be stated :

Alumina is the most valuable and distinctive constituent of clay. Its quantity regulates the physical properties of clays (plasticity, shrinking), as well as fusibility.

Silica frequently operates relatively harmful on the properties of clay. It decreases the plasticity, increases the point of fusibility, and increases the action of fluxes at high temperature. It is contained in clay, chemically as well as mechanically bound, and its analysis in latter form is necessary.

Magnesia, lime, ferric oxide, alkalies, act as fluxes, and in fact

equivalent amounts of these exert the same influence upon the fusibility. Comparatively, magnesia ranks first as a flux, lime second. Alkalies are present mostly in form of potassium oxide and are reckoned as such. Iron influences chiefly the tinge of clay, and changes the color as in the false coloring of pottery.

*Volatile matter.*—(Loss on ignition.) This is caused by the sulphur, water, carbonic acid and organic matter present. These, when present in considerable quantity, can influence the plasticity of the clay as well as the density after baking. Much stress is to be laid on the quantitative estimation of sulphur, since even minute quantities (in form of pyrite) can act harmfully. The chemical analysis of clay is divided into the empirical-technical and rational analyses.

#### A. Empirical-technical Analysis.

(a) Moisture. 2-5 grs. sample are dried to constant weight at  $120^{\circ}$ .

(b) Total loss on ignition (water of constitution, organic matter and carbonic acid).

One to 2 grams dried sample are ignited over a blast-lamp, with air access, to constant weight.

(c) Silica, alumina, ferric oxide, manganous oxide, lime and magnesia. About 1 gram finely pulverized average sample is dissolved in a platinum crucible by fusion with 6-8 times amount sodium potassium carbonate mixture.

Under no circumstances should more than ten times the amount be used. Michaelis states that it is better to use pure sodium carbonate. In this case fusion sets in at a higher temperature and after all carbonic acid has been evolved. Thereby sputtering is prevented. The fused mass is disintegrated with water, carefully acidified with hydrochloric acid, the solution is evaporated to dryness, and the silica is isolated as usual. The purity of the latter is finally tested with hydrofluoric acid. After addition of ammonium chloride, when the estimation of manganese is not taken into consideration, the iron and alumina in the filtrate are precipitated in the usual manner by ammonia. Should a separation from manganese be required, the filtrate is as nearly as possible neutralized with sodium carbonate and boiled a short time with a concentrated solution of sodium acetate or ammonium acetate.

The precipitate, which rapidly settles on removing the heat, is repeatedly decanted with hot water, to which ammonium acetate has been added. It is then thrown on the filter and washed with the water until the filtrate no longer shows traces of chlorine. The precipitate is either directly dried and ignited, or again dissolved in hydrochloric acid, reprecipitated and filtered. When greater accuracy is demanded, the filtrate is added to that previously obtained.

Special care is also to be taken in decanting and washing the precipitate, even when no attempt is made to separate manganese.

It is not considered superfluous to test the purity of the precipitate, according to Mitscherlich, by dissolving the precipitate so obtained in a large excess of a mixture of 8 parts concentrated sulphuric acid and 3 parts water. If, upon warming in a flask, flakes of silica appear, the latter is filtered, weighed, the weight deducted from that of the alumina + ferric oxide and added to that of the silica. The iron in the filtrate can be determined, after reduction with chemically pure zinc, by means of pure permanganate. Should the test of the alumina-ferric oxide precipitate be unnecessary, an aliquot portion is finely pulverized in an agate mortar and fused in a platinum crucible with bisulphate of potash, at first with a low heat and finally at a red heat. The fusion is dissolved in water, sulphuric acid is added, and the iron after reduction with zinc is titrated.

In the filtrate from the alumina and ferric oxide the manganese is eventually estimated as dioxide by adding bromine water to the cold solution, weakly acid with acetic acid, saturating with ammonia and filtering off the precipitate formed on boiling briskly. The filtrate, acidified with hydrochloric acid, is boiled down, an excess of ammonia is added, the lime is precipitated with oxalate of ammonia as usual, and the magnesia with sodium hydrogen phosphate.

(d) Alkalies. Two grams finely divided clay, mixed with a little water in a platinum dish, are covered with concentrated sulphuric acid; hydrofluoric acid is added, and the mass is warmed on a water-bath until all hydrofluoric acid has volatilized. Thereupon the sulphuric acid is almost completely expelled, and the residue is covered with hot water and hydrochloric acid. Thereby the residue may be carbonized, but at no time should it be gritty. Sulphuric acid, alumina, ferric oxide and magnesia are now precipitated with

an excess of concentrated baryta water. Excess of baryta in the filtrate is precipitated with sulphuric acid ; ammonia, carbonate and oxalate of ammonia are then added, and the whole is allowed to stand for some time. The filtrate is evaporated to dryness in a weighed platinum dish. It is then heated in an air-bath, then over a small flame to expel ammonium salts, and is finally ignited. The ignited residue is treated with water, and in event of incomplete solution it is treated in the same manner as before, with small quantities of ammonia, carbonate and oxalate of ammonia.

This operation, repeated two or three times, suffices to obtain the alkali sulphates in perfectly pure state. They are considered as potassium sulphate, from which potassium oxide is calculated.

(e) Sulphur. 5 grs. clay are mixed with powdered chlorate of potash ; concentrated nitric acid is gradually added ; the mass is slightly heated and finally boiled with repeated additions of hydrochloric acid until all nitric acid is decomposed. The excess of acid is then evaporated, water is added, and the sulphuric acid is precipitated with barium chloride.

#### B. Rational Analysis.

The purpose of this is not to determine individual constituents present, but rather to classify the same as distinct characteristic compounds. The amounts of argillaceous matter—quartz, feldspar, chalk, etc.—are determined thereby. The operation is mostly applied to pure clays for porcelain and pottery.

To do this, 5 grs. substance are softened in a porcelain dish with about 100-150 c.c. water, and boiled with addition of 2 c.c. caustic soda, whereby a fine state of division is obtained. Upon cooling, about 25 c.c. concentrated sulphuric acid are added, after which the contents of the covered vessel are kept in a state of brisk ebullition until sulphuric acid begins to volatilize. In consequence, beside the transformation of chalk to calcium sulphate, only the clay matter (silicate of alumina) is decomposed, whereas quartz and feldspar remain unattacked. The mass as obtained is separated from the greater part of the sulphuric acid and sulphate of aluminium by dilution with water and decantation. It is then twice extracted alternately with very concentrated caustic soda and hydrochloric acid. Each time it is filtered upon the same filter

upon which the whole residue is finally thrown, washed with hydrochloric acid, ignited and weighed. The residue consists only of feldspar and quartz. The loss in weight is clay and carbonate of lime. The amount of the latter is ascertained by means of a carbonic acid determination.

The mixture of quartz and feldspar is decomposed with sulphuric acid and hydrofluoric acid. In the filtrate the alumina is estimated by precipitation with ammonia, redissolving and reprecipitating, and from the result the feldspar is estimated (1 part alumina = 5.41 parts feldspar). Quartz is found by difference.

#### C. Analysis by Mechanical Means (Suspension).

Among the apparatus employed, that of Schöne claims decided preference on account of the concordant results obtained and easy manipulation. It is represented by Fig. 4. The main part is the agitator-funnel, the cylindrical portion of which, *BC*, the true suspension-chamber, is maintained in the exact proportion represented. The diameter of the lower part, *D*, must not be more than 5 mm. nor less than 4 mm. in width. The same dimensions must be preserved in the bend, *DEF*, and in the lower part of the tube, *EG*. The latter may be widened, but not narrowed, above. The exit-tube, *HJKL*, is made of barometer-tubing, the inner diameter of which should equal 3 mm. as nearly as possible. The angle at *J* should be between  $40^{\circ}$  and  $45^{\circ}$ . The exit-tube is so arranged at the deepest point on the bend, *K*, that the passing water-column is directed downward a little obliquely. It should be round, and should possess well-rounded edges and a diameter of  $1\frac{1}{2}$  mm. The arm, *KL*, is somewhat over  $1\frac{2}{3}$  m. long, and serves to measure the pressure under which the water issues at *K*. It is provided from the lowest point upward with a scale, of which 1-10 cm. is divided in mm., 10-50 in  $\frac{1}{2}$  cm. divisions, and the remainder in whole cm. divisions. The entrance-



FIG. 4.

tube, *G*, is connected, by means of a conduit, with a water-reservoir, which, with 25 l. contents, should be at the most 10 cm. high. A stopcock placed in the circuit regulates the flow. By means of a cock an upright tube, bent perpendicular, is inserted in the water-tank. This permits an entrance of air during the flow from the enclosed space and acts as a level-indicator when refilling.

With funnel and exit-tubes of the above dimensions the velocity in the suspension-chamber may be varied between 0.2-4 mm. per second. Before using the apparatus the relation between this velocity and the height of the water in the pressure-indicator (piezometer) must be determined. The velocity is equal to the issue in one second divided by squares of the cross-section of the suspension-chamber. To determine the latter a mark is made above *C*, and the water is allowed to enter up to that point.

Fifty c.c. water are then added from a pipette, and the difference in level in the suspension-chamber read off by means of a rule or cathetometer. This height divided into the 50 c.c. added gives the area of the average cross-section of the suspension-chamber. The "piezometer" levels corresponding to a velocity of .2, .5 and 2 mm. are measured and recorded for the subsequent determinations. 50 grs. of the clay selected and dried at 100°-120° are softened in water and boiled briskly at least  $\frac{1}{4}$  hour, with addition of a few c.c. caustic soda.\*

When the clay has become thoroughly disintegrated, the pasty mass is run through a sieve of 900 meshes. With the aid of a soft brush and agitation any grains of sand greater than .2 mm., as well as pebbles, roots, etc., are separated. That which has passed through the sieve and the washings from the sand are placed in a beaker and allowed to settle, after which the clear liquid is poured off and the settling are washed into the agitator funnel. Sufficient water only to raise the level in the suspension-chamber to *C* is used, and simultaneously the stopcock is opened slightly and water is admitted to prevent clogging in the base of the funnel. Thereupon water is slowly allowed to ascend the funnel, so that the

\* Clays containing lime are treated, in addition, with cold concentrated hydrochloric acid in order to remove the carbonates which frequently cement particles together. After carbonic acid evolution has ceased, the acid is completely washed out.

volume at 10 cm. is completely filled in 500 seconds. The exit-tube is then adjusted and regulated to maintain an influx of a velocity equivalent to .2 mm. in the piezometer. As soon as the receiving beaker-glass receives clear liquid, *i.e.* the water in the chamber clarifies, the particles operated upon by a current of this velocity have been removed. The receiver is then removed and the piezometer regulated for a velocity of .5 mm. Velocities under .5 mm. require an influx of about 3 liters, and a greater velocity requires 4-5 liters. The liquids in the receivers are allowed to clarify completely, and the supernatant liquid is drawn off with a siphon. The residue is washed into a porcelain dish, dried and weighed. The residue in the funnel is likewise emptied into a porcelain dish by inverting the apparatus over the dish and forcing through it a brisk current of water. The quantity is determined by siphoning, drying and weighing. The finest removable particles which take time to settle are determined by difference. Coarse sand remaining on the sieve is also weighed. The products obtained are designated as follows:

(a) Fine clay,	(Size) .01 mm.-	Current velocity, .2 mm.
(b) "Schluff" clay,	" .01 " ".02 mm.	" " ".5 "
(c) Dust,	" .02 " ".05 "	" " 2. "
(d) Fine sand,	" .05 " ".2 "	Residue in the funnel.
(e) Coarse sand,	" above ".2 "	Residue in the sieve.

#### Pyrometric Tests.

The behavior of clay at high temperatures is of vast importance in determining the shrinkage, the color, the appearance of flaws, as well as the refractoriness. To study this behavior pyrometers are necessary, in the first place, to measure the temperature obtained. For this purpose sheets of pure silver, pure gold, and alloys of the same containing 20 per cent. and upward of gold, besides gold-platinum alloys, are used, from which the following scale has been prepared :

Alloy,	80 pts. silver.	Pure silver.	Melting-point, 960° C.
		20 pts. gold.	" " 983° C.
"	60 " "	40 " "	" " 1006° C.
"	40 " "	60 " "	" " 1029° C.
"	20 " "	80 " "	" " 1052° C.
		Pure gold.	" " 1075° C.
"	95 " gold.	5 pts. platinum.	" " 1110° C.
"	90 " "	10 " "	" " 1145° C.

For higher temperatures, where alloys of gold and platinum are no longer suitable, Seger has introduced another form of pyrometer.

This consists of a series of porcelain glazes containing increasing amounts of alumina and silica, and which possess an increasing melting-point.

These substances are shaped in the form of a tetrahedron—"Seger's cones." To measure the temperature these are placed in the experimental or in the large furnace. As soon as the point of a cone is inclined in such a manner as to touch the plate upon which it is placed it has reached a corresponding temperature.

Thirty-six such cones were made and designated with increasing numbers in such a way that the melting-point of No. 1 corresponded to  $1150^{\circ}$  (approximately that of alloy of 90 parts gold and 10 parts platinum), while No. 20 represented a temperature of  $1700^{\circ}$ . Assuming now that the differences in temperature are equal to one another, then every subsequent number corresponds to an increase of  $29^{\circ}$ . For example, No. 30 corresponds to  $2000^{\circ}$  C. The compositions of these cones are given by Seger, and they can be obtained through the "Laboratorium für Thonindustrie in Berlin.\*

For lower temperatures easily-fusible cones have also been prepared to replace the expensive alloys. They range from No. 1 ( $960^{\circ}$  C.), .9, etc., to 1. ( $1131^{\circ}$  C.), making in all a total of 46.

The numbers corresponding to the temperature required for different wares are :

Bricks, tiles, terra-cotta, etc., . . . . .	to 5
Earthenware, unglazed, . . . . .	from 3 " 10
"    glazed, . . . . .	" 1
Stoneware, . . . . .	from 5 " 10
Refractory products, fire-brick, . . . . .	" 10 " 20
Porcelain, . . . . .	" 15 " 20

(a) Tests for shrinkage, color and flaws.

A stiff paste is made of the clay with about twenty times its weight of water, and this is rolled into a form of about 8 cm. length, 4 cm. width and 1 cm. thickness.

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\* The temperatures represented by each are to be found in an accompanying explanation.

On removing the models so prepared from the moulds they are provided by means of a needle-point with a longitudinal and two perpendicular lateral marks, the distance between which is measured by means of a rule provided with a vernier. The forms are allowed to dry on a wire gauze, after which the distance between marks is again measured. The shrinkage by drying is so obtained. They are then ignited with steadily increasing temperature in a muffle or furnace similar to the Deville blast-furnace, described later, until baked, during which time the temperatures are measured by means of test-cones. The tints, the formation and fusion of flaws corresponding to different temperatures, and, further, the shrinkage, are determined. An idea of the porosity can also be formed by making an ink-streak, and observing whether the ink is absorbed or whether a sharply-defined line remains.

(b) Determination of refractoriness. This is generally conducted to ascertain the melting-point of a clay, or, moreover, if the clay is to be designated as infusible.

The latter is taken into account first of all, although it may be stated that the determination of fusibility is similarly conducted.

The test of refractoriness is made in the Deville blast-furnace, Fig. 5. This consists of the hollow cylinder, *A*, made of refractive material, surrounded below by a stout wrought-iron plate. This plate has in its centre an opening of 3 cm. diameter, which, in turn, is surrounded by two rows of small openings of 6 mm. diameter at equal distances from one another. The refractory cylinder, 35 cm. high, is surrounded by an iron jacket, which is raised 8 cm. above the perforated plate, and which rests on an iron plate supported by a tripod. The space between plate and base is provided with a side-opening, *C*, of 25 mm. width, through which air under pressure is conducted from a cylindrical bellows 50 cm. in diameter. The upturned rim of the plate above is sealed with a sandy non-shrink-

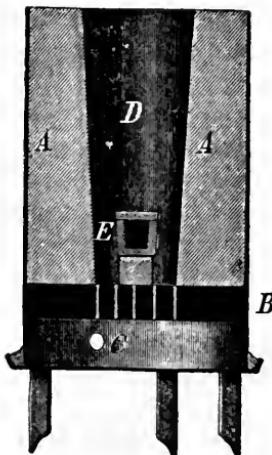


FIG 5.—Deville Oven.

ing clay to prevent escape of air. The combustion-chamber, *D*, is slightly conical, having 9 cm. diameter below and 11 cm. above. The strongly-refractory material, about 6 cm. thick, which forms the cylinder consists of about 10 cm. calcined magnesite. The upper portion is filled in with a mixture of 90 parts calcined magnesite and 10 parts good kaolin.

The clay to be examined is moulded into forms similar to those of "Seger's cones," and these are enclosed in crucibles. These crucibles are made out of strongly-ignited chamotte, consisting of equal parts alumina and fine kaolin, which is then made plastic by means of best quality kaolin. For the sake of cheapness, the supports are made of refractory chamotte, which does not melt below the "Seger cone" No. 36.

*Manipulation.*—The material under examination is made into small, three-sided pyramids of about 1 cm. base and 2 cm. height and then dried. Should organic matter be present, the models are ignited for a time at a low red heat. One or two of these pyramids are placed simultaneously with the corresponding Seger model into the crucible. Model No. 26 represents in pottery industry the fusibility of those clays which, considered as refractory materials, possess the lowest melting-point. The crucibles are 50 mm. in height, external diameter of 45 mm. and possess walls 5 mm. thick. The lid is 5 mm. thick, and the support is 45 mm. in diameter and 50 mm. high. A layer 7 mm. in height, of a mixture consisting of fine, sifted, best quality and previously suspended Zettlitz kaolin and alumina is poured in the crucible and compressed. On this layer samples and "Seger cones" are alternately placed in a circle. By lightly pressing down on them they attain the necessary hold. With a pair of long-armed iron tongs the support is placed over the large hole in the bottom plate; the covered crucibles are placed upon it and heating is begun. Firing is begun by igniting about 30 grams compressed paper and throwing it into the furnace-chamber. The bellows should not be compressed too rapidly, but about 25 times a minute. About 200 grams of charcoal, hazel-nut size, are placed on top of the paper. During this operation the paper ash is withdrawn from the furnace. When the charcoal becomes ignited a weighed quantity of broken retort graphite is thrown in. The pieces should be about

hazel-nut size, and 300 pieces should weigh about 1 kg. The compression of the bellows is increased to about 50 times per minute, and is continued until the crucible comes plainly into view. .9-1 kg., usually started with, suffice, when consumed, to have melted model 26. In order to attain higher temperature the amount of fuel with each experiment is varied from 26-40 grams. The exact amount of fuel is not capable of being determined. It depends on the heating-power of the graphite, which, however, after several experiments, can be learned. During the firing the furnace is covered with a lid. The crucibles are broken open on cooling. Since the gases in the furnace, depending on whether they possess oxidizing or reducing power, exert a great influence on the appearance of the clay, and since, in addition, the determination depends largely on the subjective judgment of the manipulator, therefore, without taking into account the behavior at lower temperatures, only the actual melting-point in Seger's temperature-units will be given.

(c) Calculation of refractoriness from the analysis :

The exact analysis of a clay is also capable of giving an insight into the degree of refractoriness.

As a standard for this the quotient of refractoriness is determined. This is done by determining the ratio of fluxing material to alumina on the one hand, and that of alumina to silica on the other, and then deriving the corresponding oxygen. Iron oxide is calculated in the form of ferrous oxide. Let  $a$  represent the oxygen in the alumina,  $b$  that in silica, and  $c$  that in the fluxing material (ferrous oxide, lime, magnesia, potassium oxide). Then the above ratios become  $\frac{a}{c} = A$  and  $\frac{b}{a} = B$ . The quotient of refractoriness

( $F$ ) then equals  $\frac{B}{A}$ . A clay is still considered refractory when this value lies between 3 and 4. The more refractory, the more these values are exceeded; the less refractory, the lower the values sink below these limits.

*Example :* The Zettlitzer kaolin, considered very refractory, and which possesses the following composition, gives the adjoining oxygen values :

Constituents.	Oxides. Per Cent.	Oxygen. Per Cent.
Silica.....	45.68	24.36 (b)
Alumina .....	38.54	18.03 (a)
Calcium oxide.....	.08	.02
Ferric oxide.....	.90	.18
Magnesium oxide.....	.38	.15
Potassium oxide.....	.66	.11
Loss on ignition .....	13.00	.46 (c)

The comparison of the fluxes with alumina taken as unity yields  $\frac{18.03}{.46} = 39.13$  (A). Alumina compared with silica taken as unity gives  $\frac{24.36}{18.03} = 1.35$  (B).

Accordingly, the formula of the clay would be  $39.13 (\text{Al}_2\text{O}_3, 1.35 \text{SiO}_2) + \text{RO}$ , and the quotient of refractoriness  $F = \frac{39.13}{1.35} = 28.98$ .

### III. Metallurgical Industry.

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#### 1. Iron.

THE following determinations are made, as a rule, for the various kinds of iron (pig iron, wrought-iron, etc.): silicon, carbon, manganese, phosphorus, sulphur. Concerning sampling, let it be stated that wrought-iron and gray pig-iron can be obtained in desired form by boring, planing or turning, whereas white pig-iron and hardened steel can be broken up with a hammer and subsequently divided in a steel mortar.

(a) Silicon. Following the method of Brown, 1-2 grs. iron—of white pig-iron and steel a larger quantity—are heated with nitric acid (sp. gr. 1.2) until everything has dissolved. 35-40 c.c. sulphuric acid (1 : 4) are then added, and the whole is heated on a sand- or water-bath until the nitric acid has volatilized. To the chilled liquid 40-50 c.c. water are then carefully added, after which it is heated to complete solution of iron salts and is filtered hot. The residue is washed first with hot water until iron is no longer detectable, and then with hot hydrochloric acid (sp.gr. 1.12) about four times, and finally with hot water to completely remove the hydrochloric acid. The moist filter is consumed in a platinum crucible at a low temperature and then ignited until the silica has become white, a point which with graphitic pig-iron is often not reached for 2-3 hours. Should the silica contain iron, it is fused with sodium-potassium carbonate.

(b) Carbon. Total carbon and graphite are usually determined, and bound carbon is calculated by difference.

(a) Total carbon. The iron is dissolved in neutral cupro-ammonium chloride solution, which is prepared by dissolving 300 grs. neutral cupro-ammonium chloride in one liter water or 340 grs. crystallized copper chloride and 214 grs. ammonium chloride in 1850 c.c. water. In the residue the carbon is determined as carbonic acid by combustion.

*Procedure.*—1 gr. pig-iron, 3–5 grs. steel or 5–10 grs. wrought-iron in pulverized condition are placed in an Erlenmeyer flask, and 50 c.c. of the above solution are added for every gram of iron.

The solution is briskly agitated at first at ordinary temperature, later at a temperature of 40° to 50°. The iron dissolves rapidly with separation of copper, which later dissolves likewise, leaving a residue consisting solely of carbon, silicide-, phosphide- and sulphide of iron. Should a precipitate of basic salts of iron form, several drops of hydrochloric acid are added to the solution. It is then filtered on an asbestos filter and subsequently on a filter pump. The first portions of the filtrate are tested for carbon, which may have passed through, by dilution with hydrochloric acid and water until transparent. It is then washed first with cupro-ammonium chloride, and later with hot water until chlorine is no longer detectable, then with alcohol, finally with ether; whereupon the precipitate is dried at a low temperature. The carbon on the asbestos filter is oxidized to carbonic acid by treatment with chromic acid and sulphuric acid. To determine the carbonic acid, apparatus for absorption of the latter is used, special care being taken to dry the evolving gases with pumice-stone, sulphuric acid and calcium chloride. In the generator of the apparatus is placed the carbon deposit, together with the asbestos-tube, which has been carefully cut with a file. 40 c.c. concentrated sulphuric acid are added, followed, when cool, by 8 grs. crystallized chromic acid. The flask is then attached to the apparatus and gently warmed. The gases evolved first pass through an upright condenser, then through the drying apparatus, and finally into the absorption vessels, which consist of two tubes containing soda-lime. The second vessel, however, is also filled about  $\frac{1}{3}$  its capacity with calcium chloride. In addition, a protecting tube filled with calcium chloride is attached. Heating is continued until evolution has ceased and sulphuric anhydride fumes appear in the condenser. An aspirator is then attached, and air, freed from carbonic acid, is drawn through the system for some time. The soda-lime tubes are then detached and weighed.

Recently methods have been proposed to determine the carbon volumetrically. That of Lunge and Marchlewski is particularly suited to this purpose. According to the latter, .5–5 grs. of the

iron under investigation are repeatedly agitated in a flask with a saturated copper sulphate solution for 1-6 hours. The flask is then connected with a condenser and a suitable gasometer and warmed with the quantity of chromic-sulphuric acid mixture necessary to insure oxidation. The authors have constructed for this purpose special forms of generators and gas burettes. An exact description of these would lead too far. They may be found in the *Zeitschrift für angewandte Chemie*, Jahrgang 1891, S. 412. The apparatus is obtainable from J. G. Cramer, in Zurich, C. Desaga, in Heidelberg, and others.

(β) Graphite. 4-5 grs. iron are dissolved by warming with dilute hydrochloric acid. The residue is filtered on an asbestos bed. The latter is washed with hot water until the filtrate, on addition of silver nitrate, no longer opalesces. It is then washed 4-5 times with dilute caustic potash, followed by alcohol, to remove potash, and finally with ether. After drying, the graphite is oxidized like the total carbon with chromic acid and sulphuric acid.

(c) Manganese. Of the many methods proposed for this determination, that of Volhard only will be described here.

*Principle.*—If to a neutral or slightly acid solution of a manganese salt, permanganate of potash be added at 80° C., a complete precipitation of the manganese ensues.

The equation  $Mn_2O_7 + 3MnO = 5MnO_2$ , originally proposed for this method, is incorrect under the conditions given, according to Volhard, inasmuch as a precipitate containing manganous oxide,  $5MnO_2 \cdot MnO$  is formed. If, however, a solution of a zinc, lime or magnesium salt be added, a peroxide containing zinc oxide, lime or magnesia will be precipitated.

Observing these facts, manganese in iron may be determined by adding zinc oxide to the solution containing all the iron in the *ic* and all manganese in the *ous* condition. Ferric oxide is precipitated, while an equivalent amount of zinc is dissolved. The solution is then titrated with permanganate of potash.

*Standardization.*—The permanganate is standardized on iron in the usual manner, and is then calculated into manganese units (of manganous oxide) by use of the equation  $10Fe(= 2KMnO_4) = 3Mn$ .

*Experiment.*—About 4 grs. sample (less, if it contain much manganese) are dissolved in nitric acid (sp. gr. 1.2); the solution

is evaporated to dryness, and the residue is heated for about 1 hour on a sand- or air-bath. Thereupon it is dissolved in warm hydrochloric acid; 20 c.c. sulphuric acid (1 : 1) are added, and the whole is heated until sulphuric acid volatilizes. It is then taken up with water and washed into a 500 c.c. graduated flask. The excess of acid is nearly neutralized with sodium carbonate, and, while being agitated, freshly calcined zinc oxide, suspended in water, is added until the solution, which gradually turns dark brown, suddenly congeals from separation of the entire ferric oxide. Water is then filled in to the mark, and 100 and 250 c.c. respectively of the clear filtrate are withdrawn for titration with permanganate, which should be approximately  $\frac{1}{10}$  normal.

The solution to be titrated is heated to about 80° C. It is vigorously shaken while the permanganate is introduced until the liquid above the flocculent precipitate, which settles rapidly, is of a pink color. It is then boiled, and when the color has disappeared, more permanganate is added until a permanent color remains.

*Modification by Ulzer and Brüll.\**—In order to overcome the not inappreciable difficulty of detecting the end reaction of the titration with permanganate, 20 c.c. of a .5 per cent. solution of hydrogen peroxide may be added to the above solution, which has been freed from ferric oxide by means of zinc oxide and filtered.

This is followed by the addition of caustic soda as long as a precipitate forms, after which it is boiled. Manganese is precipitated as  $5\text{MnO}_2\cdot\text{MnO}$ . Upon cooling, oxalic acid of known strength is added, together with pure dilute nitric acid. It is then digested at a low heat until the precipitate redissolves, after which it is heated almost to boiling, and the excess of oxalic acid is titrated with permanganate.

(d) Phosphorus. To 1–5 grs. iron nitric acid (sp. gr. 1.2) is added, and heat is applied to dissolve it finally. Then to fully oxidize the phosphorus it is boiled with 25 c.c. of a 1 per cent. potassium permanganate solution. An aqueous solution of 8–10 grs. ammonium chloride is added to dissolve the manganese peroxide formed.

The solution, clarified by reheating, is evaporated to dryness,

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\*. Contribution of the K. K. Technol. Gen. Mus., Jahrg. 1895, p. 312.

and the residue dissolved by treating with 10–20 c.c. concentrated hydrochloric acid. The solution is evaporated to syrupy consistency and 10 c.c. nitric acid are added, followed, after a few moments, by hot water. It is then filtered, washed with water containing nitric acid, nearly neutralized with ammonia, though the liquid is kept clear. The solution, now about 100 c.c., is heated to 70°, and precipitated with 25 c.c. molybdate solution. After

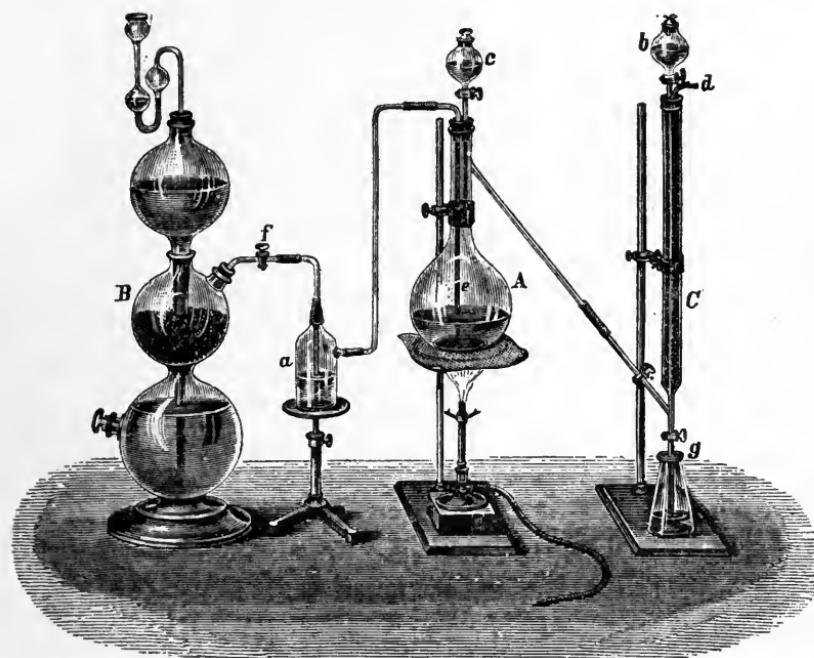


FIG. 6.—Apparatus for Determining Sulphur.—Johnston and Landolt.

standing for two hours at a temperature of 40° C. the liquid is filtered off and the precipitate is washed with dilute molybdate solution, containing nitric acid, as long as iron is present. It is then dissolved in ammonia, and precipitated with magnesia mixture in the usual manner.

(e) Sulphur. Using the less recent directions of Johnston and Landolt, 5 grs. finely-divided iron are introduced into the flask, *A*, of the accompanying apparatus (Fig. 6). Bromine-hydrochloric

acid mixture is allowed to flow from *b* into the tube, *C*,\* which is filled with glass beads. The stopcock, *g*, is closed during the above operation. 5-10 c.c. concentrated hydrochloric acid are run into the flask from the funnel, *c*. The hydrogen sulphide generated is oxidized by the bromine to sulphuric acid. When the bromine-hydrochloric acid mixture decolorizes, it is run into the flask beneath, and is replaced by fresh solution. When the evolution of gas in *A* ceases, more hydrochloric acid from *C* is added, and the flask finally heated, while carbonic acid is run through, which has been washed with an interposed wash-bottle containing mercuric chloride, to absorb any hydrogen sulphide.

After having been brought to boiling, the bromine solution is allowed to flow into the flask, the glass beads are washed with water, and the solution is evaporated in a porcelain dish. After the bromine and the excess of hydrochloric acid have volatilized, the liquid is diluted with water, filtered, and the sulphuric acid is precipitated with barium chloride. Bromine and hydrochloric acid must, of course, previously be tested for sulphuric acid. Instead of the disagreeable bromine-acid mixture, an ammoniacal hydrogen peroxide solution, entirely free from sulphuric acid, may be used.

According to the new and popular procedure of Schulte,† 10 grams granulated sample are placed in the flask, *A*, of the accompanying apparatus (Fig. 7). The receiver, *F*, contains 45-50 c.c. of a mixture of 25 grs. cadmium acetate and 200 c.c. glacial acetic acid diluted to 1 liter. Another portion of 10 c.c. of this solution is placed in the cylindrical vessel, *H*. The apparatus is then arranged as seen in the figure. Thereupon, 200 c.c. hydrochloric acid (1 : 2) are placed in the funnel, *B*, and allowed to slowly descend into the flask, *A*. By slowly heating the flask, the iron is brought into solution in about 1½-1¾ hours. It is now boiled until all hydrogen sulphide has been driven out of *A*, which will be the case when, after 1-2 minutes, the clatter, due to steam condensation, is heard in the receiver. The hydrogen sulphide evolved produces a precipitate of cadmium sulphide in *F*, while under normal conditions no hydrogen sulphide will enter *H*. In any case,

\* In place of the tube, Winkler absorption coils, containing bromine and hydrochloric acid, may be advantageously used.

† Stahl u Eisen, Jahrg. 1896, S. 865.

the stopper, *E*, is raised, and a quantity of 5–7 c.c. copper sulphate, containing sulphuric acid, is added. This is prepared by dissolving 80 grs. crushed copper sulphate in 750 c.c. water. 175 c.c. concentrated sulphuric acid are added, the whole is diluted to one liter, and filtered. Upon the addition of this solution, a rapid and complete transformation of cadmium sulphide to copper sulphide takes place. This may be hastened by agitation. The separated copper sulphide is filtered off and estimated by conversion into oxide or subsulphide. One equivalent of sulphur is reckoned

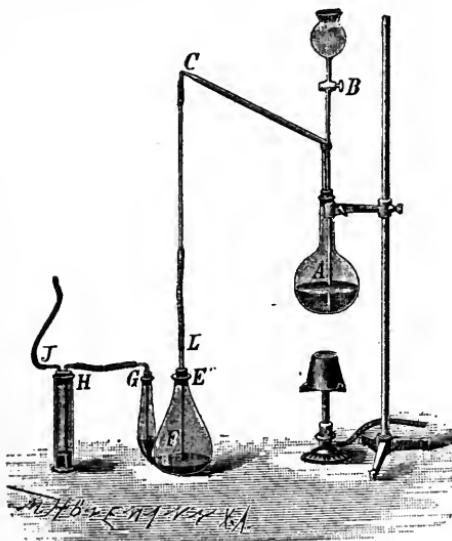


FIG. 7.—Apparatus for Determining Sulphur.—Schulte.

for every equivalent of copper found. Therefore 63.5 copper ( $= 79.5$  copper oxide  $=$  same amount of cuprous sulphide)  $= 32$  sulphur.

Should a small precipitate of cadmium sulphide perhaps appear in *H*, the two liquids are united and simultaneously precipitated with copper sulphate.

## 2. Zinc Blende.

The most important determinations in this are sulphur, zinc and lead. The following methods, used in most zinc works, are preferable :\*

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\* Lunge, Taschenbuch für Soda-fabrikation, etc.

(a) Total sulphur. .5 gr. of impalpable sample is covered with about 20 c.c. of a mixture of 3 parts concentrated nitric acid and 1 part concentrated hydrochloric acid, or else with a saturated bromine-hydrochloric acid mixture, and allowed to stand over night, after which it is evaporated almost to dryness and several c.c. hydrochloric acid introduced, followed by 50 c.c. hot water. It is then filtered and precipitated with barium chloride.

(b) Zinc. According to the modified Schaffner process, 2.5 grs. finely-powdered sample are treated with 12 c.c. fuming nitric acid in an Erlenmeyer flask, at first in the cold and finally at a low heat, until the red fumes have disappeared, 20-25 c.c. conc. hydrochloric acid are added, and the liquid is evaporated to dryness on a sand-bath. The residue is taken up with 5 c.c. hydrochloric acid and a little water and heated to dissolve soluble portions. Then 50-60 c.c. water are added, and heat is applied again to maintain it at 60°-70° C. Everything should dissolve but gangue and separated sulphur. A brisk current of hydrogen sulphide is conducted into the solution, accompanied by a subsequent gradual addition of 50-100 c.c. cold water while the liquid is being agitated, in order to completely precipitate all lead and cadmium. Excessive dilution and too prolonged an addition of hydrogen sulphide should be avoided. The precipitate is filtered and washed with 100 c.c. water containing hydrogen sulphide and 5 c.c. hydrochloric acid until a drop of the filtrate no longer shows a trace of zinc when treated with ammonium sulphide. Filtrate and washings are boiled to remove hydrogen sulphide, and the iron is oxidized by addition of 5 c.c. conc. nitric acid and 10 c.c. hydrochloric acid. After partially cooling, the liquid is poured into a graduated flask of 500 c.c. capacity, and 100 c.c. ammonia (sp. gr. .9-.91) and 10 c.c. saturated ammonium carbonate solution are added. In the meantime an ammoniacal zinc solution of known strength is prepared by dissolving a quantity of chemically pure zinc, approximating the amount of zinc contained in the ore, in a flask of 500 c.c. capacity, by the addition of 5 c.c. nitric acid and 20 c.c. hydrochloric acid and diluting with about 250 c.c. water, 100 c.c. ammonia, and 10 c.c. of the above ammonium carbonate solution are added; the solution is agitated and allowed to stand. In the presence of manganese an addition of 10 c.c. hydrogen peroxide should precede

that of ammonia. After thoroughly cooling, both flasks are filled to the mark, and the contents of the one containing the ore are filtered through a dry ribbed filter. In titrating 100 c.c. of each solution, ore and standard are placed in thick-walled cylinders and are diluted with 200 c.c. water. For titration a concentrated solution of commercial crystallized sodium sulphide is very suitable. The latter is dissolved in 10-20 volumes of water, and should represent approximately .005-.01 gr. zinc per c.c. This solution is run alternately from two adjoining 50 c.c. burettes into the solutions, and, in fact, 2-3 c.c. less than required at first.

Drops of the stirred liquids are then placed on a strip of sensitive lead-acetate paper with a thin glass rod. After 15-20 seconds the drops are washed off, the addition of sodium sulphide solution is continued, and the tests with lead-acetate paper are repeated until after an equal period faint but distinct tints of equal intensity appear. It is desirable to contrast the first result, usually approximate, with two or three more. At any rate, the end reactions in both cylinders must be uniform in both vessels and the readings must be made within .05 c.c.

Let the amount of zinc in the standard solution = a, the number of c.c. sodium sulphide used in titrating 100 c.c. standard solution = b, and the number used in titrating 100 c.c. solution containing ore (= .5 gr. ore) = c; then the percentage of zinc =  $\frac{40 ac}{b}$ .

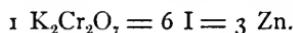
In very exact determinations a quantity of ferric chloride corresponding to that in the ore solution is added to the standard solution to compensate for a possible precipitation of zinc by the ferric hydrate.

(c) Lead. The precipitated sulphides in b are, if necessary, digested with a fairly concentrated solution of sodium sulphide, diluted and filtered. The residue, plus filter-paper, is dissolved in dilute nitric acid, evaporated with an excess of sulphuric acid, and the lead is determined as lead sulphate.

### 3. Zinc Dust.

The following method of Drewsen, modified by Fraenkel, determines the reducing value only, and therefore small quantities of iron and cadmium present are calculated as zinc. The method

depends on the fact that by the action of sulphuric acid on zinc, in the presence of an excess of bichromate of potash, a part of the chromic acid is reduced to chromic oxide. The unaltered chromic acid is determined iodometrically, and the zinc is calculated from the difference. A  $\frac{1}{2}$  normal potassium bichromate solution, containing 24.58 grs. of the pure salt in a liter, and a  $\frac{1}{2}$  normal hyposulphite solution are suitable. The latter is exactly standardized on the former. In operating, approximately .5 gr. zinc dust is placed in a dry flask of about  $\frac{3}{4}$ -liter capacity provided with a stopper. 50 c.c. bichromate solution, next 5 c.c. dilute sulphuric acid (1 : 5), are added, and the mixture is agitated. After about 5 minutes 10 c.c. more sulphuric acid are added, and the whole is shaken for 10 minutes, when complete solution usually ensues. In order to estimate the chromic acid yet present, 40 c.c. iodide of potassium solution (1 : 10) are added, followed by additional 20 c.c. sulphuric acid. Separation of considerable iodine ensues. ( $2\text{CrO}_3 = 6\text{I}$ ). After dilution with 400-500 c.c. water, the iodine is titrated with hyposulphite. To determine the end reaction with precision, hyposulphite solution is added to the brown iodine solution until the latter becomes yellow-green in color. Starch paste is added at this point, whereby the liquid turns deep green. By continued careful titration the color changes gradually into a deep blue until finally the comparatively light-green chromic salt is obtained, at which point the titration is complete. With a little practice, a sharp end reaction is go ten. The difference between the quantity of bichromate solution added and the quantity of hyposulphite solution used in back titration gives the chromic acid reduced by the zinc, from which the zinc can be calculated.



#### 4. Crude and Refined Copper.

Great stress has been recently laid on the technical examination of the chemical composition of the kinds of copper named. Certain specifications in this direction are required; for example, for railroad consignments. In consequence, various kinds of copper are often subject to quantitative chemical analysis. The analysis offers considerable difficulty when contaminations, usually present in small

amount, are present in quantity. When an exact total analysis is desired,\* the very reliable method of Fresenius seems to be the simplest one. The method is given here, with a few slight modifications by Fraenkel.

The foreign elements which are to be determined are: Silver, lead, arsenic, antimony, tin, bismuth, iron, cobalt, nickel, zinc, sulphur, phosphorus and oxygen. The determination of gold may usually be neglected. Copper is calculated with sufficient accuracy by difference.

100 grs. copper turnings or shavings are taken for the analysis, and, after separation of particles of iron by means of a magnet, are dissolved in nitric acid (sp. gr. 1.2). Solution had best be conducted in a beaker of about 1 liter capacity. The acid is gradually added and warmed toward the end, to effect complete solution. It is filtered, after dilution with water, into a graduated 2-liter flask, washed with hot water, and the flask (*A*), not yet filled to the mark, is stood aside.

The residue is washed from the filter into a porcelain crucible and evaporated to dryness; the filter ash is added and fused with a mixture of soda and sulphur. The chilled fusion is lixiviated with hot water, filtered into a graduated flask of 200 c. c. capacity and washed with water to which some sodium sulphide has been added. The filtrate (*B*), which is diluted to the mark, is likewise corked up and preserved. The residue (*C*), together with the filter-paper, is warmed with nitric acid (1 : 1), diluted with water, filtered and added to flask (*A*), which is then filled to the mark. From the contents of this flask 1000 c.c. are removed for the determination of silver, lead, bismuth, arsenic, tin, antimony, iron, nickel, cobalt and zinc, and the remaining liquid is preserved. This 1000 c.c. represents one-half the original amount of substance taken. It is placed in a beaker, about 4 drops conc. hydrochloric acid are added, and warmed and stirred, in case turbidity ensues, until the liquid clarifies. The separated silver chloride is filtered off and washed. The silver is determined as usual. The lead is determined by adding 85 grs. conc. sulphuric acid to the filtrate,

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\* For the simple estimation of the copper, the electrolytic method, by all means, answers the purpose best.

evaporating on a water-bath until nitric acid is completely expelled, dissolving the separated sulphate of copper in water by warming, and filtering off the insoluble sulphate of lead. The latter is washed first with water containing sulphuric acid, and then over a separate receiver with dilute alcohol. The lead is then determined in the usual manner.

The filtrate from the lead sulphate is heated and then placed in a previously weighed flask (*D*) of about 5 liters capacity. Sufficient hot water is added to bring the total volume to 3-4 liters. About 50 c.c. conc. hydrochloric acid are added, and a brisk continuous current of hydrogen sulphide is conducted in, until complete precipitation is indicated by the rapid settling of the precipitate and a perfectly colorless supernatant liquid. The precipitate (*E*) contains all the copper, bismuth, arsenic, antimony and tin. Iron, nickel, cobalt and zinc remain in solution. Flask, solution and precipitate are weighed; the weight of the flask is deducted and the weight of liquid and precipitate thereby ascertained. The weight of precipitate is found by calculating the copper contained therein into copper sulphide. If this be deducted also, the weight of liquid alone is obtained. As soon as the precipitate has well settled, as much of the clear liquid as possible is drawn off with a siphon. If the remaining liquid, precipitate and flask be now weighed together, the difference between it and the former weight gives the weight of liquid siphoned off. By simple proportion the corresponding quantity of original substance contained therein can be calculated. This solution, filtered if necessary, serves for the determination of iron, nickel, cobalt and zinc. For this purpose it is evaporated as far as possible in a porcelain dish on a water-bath and the excess of sulphuric acid is volatilized over a naked flame. The residue is heated with water and nitric acid, filtered, treated with an excess of ammonia, and the precipitate formed is dissolved in hydrochloric acid and reprecipitated with ammonia. The operation is repeated if necessary, and the precipitate is finally weighed as ferric oxide. To the collected filtrates more ammonia is added, followed by acetic acid to slight acid reaction. Hydrogen sulphide is conducted into the heated solution, whereby cobalt, nickel and zinc are precipitated. These are filtered off, dried, removed as far as possible from the filter, and dissolved in nitric acid and a little

hydrochloric acid. The filter ash is added, the liquid is evaporated on a water-bath, taken up with water and a little hydrochloric acid, and then exactly neutralized with sodium carbonate, using methyl-orange as indicator. A slow current of hydrogen sulphide is now led in for a brief period. A few drops of dilute, preferably very weak, alkaline sodium acetate solution are added, whereby an appreciable darkening of the precipitate should not ensue. A very slow current of hydrogen sulphide is again led in for a few minutes, and the zinc sulphide formed is allowed to settle for a few hours. It is filtered in a double filter, washed with water containing hydrogen sulphide, and the zinc is determined as sulphide in the usual manner.

The filtrate from the zinc is best completely evaporated to expel hydrogen sulphide. The residue is taken up with hydrochloric acid and water, filtered if necessary, and the cobalt and nickel are then precipitated with an excess of caustic potash. They are first of all determined together. Should a separation be desired, which as a rule will not be required on account of the preponderance of nickel, one of the usual methods is employed.

To the residual liquid and precipitate (*E*) in flask (*D*) potassium or sodium hydrate is added to slight alkaline reaction. A sufficient quantity of light yellow potassium or sodium sulphide solution is then added, together with 100 c.c. (= one-half) of the liquid in flask (*B*). The flask is then placed in a warm place, and frequently agitated to bring all sulphides of antimony, tin and arsenic into solution. It is then diluted to 3-4 liters with water and weighed, and as much as possible of the clear liquid is withdrawn. The remainder, together with flask and sediment, is weighed, and the amount of copper corresponding to the liquid withdrawn is calculated as before. The flask and precipitate are preserved.

In order to estimate antimony, tin and arsenic, the liquid is filtered, if necessary, and acidified with hydrochloric acid. The sulphides of these metals and much sulphur are precipitated. These are allowed to settle for a time, and are then filtered and dried. Thereupon precipitate and filter are placed in a flask and extracted with carbon disulphide to free from the greater part of the sulphur. The solution is filtered and the residue is warmed with dilute ammonium sulphide, whereby the sulphides dissolve. After this

has been filtered and the filter has been thoroughly washed it is warmed, and pure hydrogen peroxide is added until the color has disappeared and the sulphur has been thoroughly oxidized. It is now evaporated to dryness in a spacious porcelain dish and oxidized with fuming nitric acid. The latter is expelled as far as possible, and potassium hydrate is added to distinct alkaline reaction, after which the whole is washed into a large silver crucible. A few pieces of stick caustic soda are placed in the crucible, which is heated carefully in a sand-bath until the water has been completely expelled. The residue is then gradually heated to continued fusion, and finally over a naked flame. The crucible contents, now perfectly clear, are lixiviated with water until the insoluble particles have separated as a powder, when about  $\frac{1}{2}$  the volume of alcohol is added. The crucible is covered, and the contents are occasionally stirred during the 24 hours in which it is allowed to stand. The undissolved sodium antimonate is filtered and washed with dilute alcohol (1:1), to which a few drops of sodium hydrate solution have been added. Stannate and arsenate of sodium remain in the filtrate (*F*). The precipitate of sodium antimonate on the filter is repeatedly covered with a warm solution of tartaric acid in dilute hydrochloric acid until all has dissolved. The solution is diluted, heated and precipitated with hydrogen sulphide. Orange sulphide of antimony forms. Should the precipitate be rendered dark from silver sulphide arising from the crucible, it is redissolved by warming with ammonium sulphide, filtered from the sediment and reprecipitated with hydrochloric acid. The hydrogen sulphide is expelled by conducting into the flask a current of carbonic acid. It is then filtered on a previously dried and weighed filter, after which it is dried and weighed. To expel the last traces of water and sulphur when large quantities of antimony sulphide are concerned, an aliquot portion of the dried precipitate is placed in a porcelain boat, which is introduced into a glass tube and moderately heated. Pure dark-gray trisulphide of antimony is thus obtained. With small quantities it suffices to wash the dried precipitate on the filter repeatedly with carbon disulphide, dry and weigh.

Hydrochloric acid is added to filtrate (*F*) to acid reaction. Thereby a white precipitate of arsenate of tin now and then appears. Without taking notice of this, the tin and arsenic are

precipitated with a current of hydrogen sulphide. These are filtered on a dried and weighed filter, washed with hydrogen sulphide water, dried and weighed. A separation of tin from arsenic in the precipitate, which usually contains a considerable amount of sulphur, is conducted in the following way: An aliquot portion of the same is placed in a bulb tube bent at a right angle on one side. The straight side is attached to a hydrogen sulphide generator by means of a calcium chloride drying tube. The bent part is connected by a rubber stopper to a Peligot tube filled with ammonia (about 1 : 2). This tube, finally, may be attached to a second absorption vessel. The bulb is then heated in a current of hydrogen sulphide. Sulphide of arsenic and sulphur which are evolved collect in the ammonia, while sulphide of tin remains in the bulb. The bulb-tube is detached and heated strongly in a current of air, which is conducted through. The sulphide of tin is thereby changed to oxide, and this is weighed on cooling. The tin is calculated from it.

The solution of sulphide of arsenic is washed into a beaker, acidified with hydrochloric acid, chlorate of potash is added, and the liquid is warmed moderately. Sulphide of arsenic dissolves. Any sulphur remaining is filtered off. The arsenic in the filtrate is determined as magnesium pyroarsenate in the usual manner, and from it the arsenic is calculated. Bismuth is determined by repeatedly adding a large quantity of water containing sodium sulphide to the remaining liquid and precipitate in flask (*D*), shaking, and drawing off as much liquid as possible. The residue is covered with hydrochloric acid, nitric acid is gradually added, and the whole is allowed to stand in a warm place. A gradual solution of the precipitate takes place, with separation of pure sulphur. Too energetic action causes retention of copper sulphide. The sulphur is filtered off, washed, and the solution is evaporated repeatedly with hydrochloric acid. When the latter is almost completely expelled, water is added, and the small amount of residue remaining is filtered off. The latter consists principally of basic bismuth chloride. To purify the same, it is dissolved in dilute hydrochloric acid, treated with caustic potash to alkaline reaction, potassium cyanide is added, and the bismuth is precipitated with sodium sulphide, while sulphide of copper remains dissolved in the cyanide

of potash. The precipitate is thrown on a previously dried and weighed filter, repeatedly washed with carbon disulphide, and weighed as sulphide of bismuth.

Sulphur is determined by adding ammonia to 400 c.c. of the liquid remaining in (*A*), until the greater part of the free nitric acid has been neutralized, and after the addition of a few drops of barium nitrate solution is allowed to remain in a warm place. In the presence of appreciable traces of sulphur, probably contained in the form of sulphurous acid in the copper, a small precipitate of barium sulphate is formed which is filtered and weighed.

In another 400 c.c. solution still in flask (*A*), the phosphorus is determined.

To accomplish this the liquid is repeatedly evaporated with hydrochloric acid to expel nitric acid. The residue is dissolved in hot water, placed in a weighed flask of 2 liters capacity, and diluted with hot water to about 1200 c.c. This solution is completely precipitated at about 70° C. with hydrogen sulphide. The sulphides are allowed to settle and as much clear supernatant liquid as possible is drawn off. Flask, remaining liquid and precipitate are weighed, and, as before, the corresponding amount of copper in the separated liquid is calculated. The solution is filtered, evaporated to small bulk with repeated additions of nitric acid, and the phosphorus is determined in the usual manner. (See also Chapter V., Fertilizers.) The method of Hampe is used to determine, in the bullion, the oxygen which is combined partly with metals and partly with sulphur. The thoroughly cleaned copper is first filed. The filings are sieved through a hair sieve and the iron particles are withdrawn by means of a magnet. The powder is next boiled with dilute caustic potash to rid it of traces of fat, etc. The liquid is poured off, and the powder is washed and hurriedly dried.

The estimation of oxygen is calculated by loss of weight upon ignition in a current of hydrogen. A hard glass bulb tube, drawn out at both ends, is suitable for this purpose. It is first heated in a current of dry air and then allowed to cool. It is weighed; 10-20 grs. dry copper powder are thereupon placed in the tube, which is reweighed. Dry carbonic acid from a Kipp generator is then conducted through the tube. The generator is set in action two hours before use, and to purify and dry the carbonic acid it is led through

the following system: A solution of bicarbonate of soda, a tube filled with lumps of bicarbonate, a wash-bottle containing silver nitrate solution, a tube containing pumice-stone saturated with the latter solution, a wash-bottle containing conc. sulphuric acid, and finally a calcium chloride tube. The carbonic acid is allowed to pass through the tube containing the copper for five minutes, after which it is very moderately heated to free from all traces of water. A sublimate of arsenic acid will form when the heat applied is too strong. Pyrogenous products should not form. Upon cooling in carbonic acid, the latter is replaced by air and the tube is weighed. The loss of weight should equal only a few milligrams. A very slow current of pure hydrogen is then conducted over the copper. Thereupon the latter is at first moderately heated, and later to glowing, for about fifteen minutes. During the application of heat, water forms, whereas, with impure copper, a sublimate of arsenic, antimony and lead, forms in the bulb and adjacent to it. This sublimate should in no case issue from the tube. Therefore the tube should be drawn out sufficiently long, and the hydrogen current should be correspondingly slow. When the copper contains sulphurous acid, some hydrogen sulphide is evolved with the steam. In order to estimate its quantity, the gases are led through an alkaline lead solution or a bromine-hydrochloric acid mixture, and the sulphur is estimated from the sulphuric acid formed. After the copper has thoroughly cooled in hydrogen, dry air is again conducted through and the tube is weighed. The loss in weight, less the sulphur evolved as hydrogen sulphide, gives the amount of oxygen present.

## IV. Alloys.

### 1. Phosphor-Bronze.

This usually contains copper, tin and phosphorus, and frequently also lead and zinc. The presence of other constituents, however, like arsenic and iron, is not excluded,\* on account of which a qualitative analysis should always be conducted first. 3 grams of the broken-up alloy, taken for quantitative analysis, are covered with water, and nitric acid is carefully added. Heat is generated, and decomposition takes place. It is brought to a finish by heating with a small flame. It is evaporated to dryness in a porcelain dish, dissolved in nitric acid, and water is added, after which it is filtered and washed out with hot water (= residue A and filtrate B).

Residue A contains all the tin, together with all phosphorus (as phosphate of tin), some copper and some of the lead. It is ignited and weighed. Thereupon it is fused in a porcelain crucible with carbonate of soda and sulphur. The fusion is lixiviated with hot water. The small residue is filtered off, and estimated either directly as subsulphide of copper by ignition with sulphur in an atmosphere of hydrogen, or else, if necessary, a separation of copper from lead is carried out by means of sulphuric acid in nitric acid solution. The filtrate containing the phosphoric acid and tin is acidified with hydrochloric acid. The sulphide of tin is filtered off, the filtrate evaporated to dryness on a water-bath, and taken up with nitric acid. The phosphoric acid is precipitated with molybdate solution, and the determination is continued in the usual manner. The copper, calculated into cupric oxide, plus the phosphoric anhydride formed from the phosphorus, is deducted from the total residue, and the remainder is calculated as oxide of tin.

The filtrate B, after addition of sulphuric acid, is evaporated to dryness, to precipitate lead, and the sulphuric acid completely

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\* No account of the presence of these is taken in the following method of quantitative analysis.

expelled. The residue is then taken up with water, washed with water containing sulphuric acid, then with alcohol, and is finally ignited and weighed. Filtrate from the lead sulphate is placed in a 250 c.c. graduated flask, and diluted to the mark. In one portion of 50 c.c. the copper is estimated as sulphide by means of hydrogen sulphide, while in the remaining 200 c.c. the metals present in less quantity may be determined. For this purpose copper is precipitated with hydrogen sulphide, and filtered off. The filtrate is evaporated to dryness, taken up with a few drops of hydrochloric acid, neutralized exactly with sodium carbonate, and hydrogen sulphide is run in. Sulphide of zinc is precipitated. Upon addition of a few drops of a dilute solution of sodium acetate and renewed addition of hydrogen sulphide, the precipitation is completed. The precipitate is allowed to stand for a time, filtered, and determined as zinc sulphide by ignition with sulphur in a current of hydrogen. To the copper contained in the filtrate B, that which was contained in residue A must be added. The same holds good for any lead found in the residue.

## 2. White Metal.

This contains tin, as a rule, as chief constituent, together with antimony and also zinc. Copper and lead are frequently present in minute quantities, although sometimes in large quantities. Arsenic, mercury, nickel and iron may be present. The quantitative analysis covering the presence of tin, antimony, copper, lead and zinc will be described.

1-2 grs. alloy are dissolved in nitric acid, as previously described, evaporated nearly to drynesss, taken up with dilute nitric acid, filtered, and washed with water containing ammonium nitrate. (Filtrate A. Residue B.)

Filtrate A contains copper, lead and zinc, whose separation is conducted as given under Phosphor-Bronze.

Residue B contains all tin and antimony, besides small quantities of copper, lead and zinc. It is dried, ignited and weighed. A weighed portion of the same is fused with soda and sulphur, and the fusion is lixiviated with water. Should the residue be small, it may be directly ignited with sulphur in a current of hydrogen, and considered as the sulphide of one of the three metals, copper, lead

and zinc, depending on the predominance of one or another as shown by the qualitative tests or the quantitative analysis of filtrate A. Should there be considerable residue, it is dissolved in hot dilute nitric acid, and the individual constituents are separated and determined. The amount of these (in form of oxides) is deducted from the substance used for fusion, whereby tin oxide and antimony oxide ( $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_4$ ) remain. These are recalculated from the aliquot portion used on the total residue. In order to separate tin and antimony, another portion of the residue B is fused with caustic soda in a silver crucible, and the fusion is lixiviated until the insoluble portion is powdered. One-half volume of alcohol is added, and allowed to stand 24 hours with repeated stirring. It is then filtered off and washed with dilute alcohol (1 : 2). The sodium antimonate remaining in the filter contains a small quantity of copper, whereas traces of lead or zinc will remain in solution with the tin, and can be precipitated by careful addition of sodium sulphide. After filtration from this minute precipitate, hydrochloric acid is added to precipitate tin sulphide, which is quantitatively estimated as tin oxide by careful oxidation and ignition with ammonium carbonate. If this be calculated on the total residue, and subtracted from the sum of the oxides of tin and antimony previously found, there remains the antimony tetroxide, from which antimony is calculated.

### 3. Iron Alloys.

Iron is alloyed with other substances besides those mentioned under the investigation of iron, in order to impart to it certain properties, principally hardness and toughness. Some of these substances are chromium, tungsten, titanium, aluminium and nickel. For instance, there is contained in tungsten steel 9 per cent. W.; in chromium steel, 2-4 per cent. Cr.; in ferro-chrom, 29-49 per cent. Cr.; in ferro-aluminium, 6.8-10 per cent. Al., and in nickel steel, 8-10 per cent. Ni. With reference to chromium and nickel estimations, ferro-chrom and nickel steel serve as illustrations of such alloys.

*Ferro-chrom.*—1-4 grs. of sample, powdered as fine as possible, are boiled  $\frac{1}{4}$  hour in a large beaker with 500 c.c. water and 50 c.c. sulphuric acid (1 : 1). Usually all dissolves. Should a residue remain, however, after continued heating, it is filtered off, washed,

incinerated in a platinum capsule, and fused with a mixture of two parts fused borax and three parts soda for three hours at a high heat, preferably in a muffle. The fusion is dissolved in water, acidified with sulphuric acid, and added to the first filtrate. The united filtrates are brought to boiling, and a concentrated permanganate solution is added to the same until red coloration sets in. The excess of permanganate is reduced with manganous sulphate, after which it is washed into a liter flask filled to the mark after cooling, well shaken, and filtered through a ribbed filter. An aliquot part of this solution, which is colored yellow in presence of the smallest quantities of chromium, is treated with 50 or 100 c.c. ferrous ammonium sulphate solution (containing 20 grams of the salt and 10 c.c. sulphuric acid (1 : 1) to the liter), after which the excess of ferrous salt is titrated back with  $\frac{1}{10}$  normal permanganate. At the same time the same quantity of ferrous ammonium sulphate solution is titrated with permanganate, and from the quantity of the latter now used the first is deducted. The difference represents the ferrous oxide oxidized by the chromic acid from which chromium can easily be calculated.  $2\text{CrO}_3 = 6 \text{Fe O}$ .

*Nickel steel.*—2-4 grs. sample are dissolved in nitric acid (sp. gr. 1.2). After dissolving, 10-20 c. c. sulphuric acid (1 : 1) are added, and the whole is evaporated until sulphuric acid begins to volatilize. The residue is dissolved in water, and the solution is gradually poured into a 500 c.c. flask in which 50 c.c. sulphate of ammonium solution (containing 500 grs. of the salt in a liter of water) and 130 c.c. conc. ammonia have previously been placed. It is then diluted to the mark, well mixed, and filtered through a ribbed filter. Two hundred and fifty c.c. of the filtrate are taken, and in this the nickel is determined either electrolytically or by precipitation with ammonium sulphide, or hydrogen sulphide,\* in a solution slightly acidified with acetic acid. In case copper was present in the nickel steel, it will be found in the ammoniacal solution. The copper, in the solution strongly acidified with hydrochloric acid, may be removed with hydrogen sulphide. Estimation of nickel is then conducted with the filtrate.

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\* In the latter case the precipitate of nickel sulphide is dissolved in hydrochloric acid, with addition of nitric acid or potassium chlorate, and then precipitated with caustic potash. It is finally transformed into metallic nickel by reduction in a current of hydrogen.

## V. Fertilizers.

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THESE may be divided into three groups, according to their active constituents: 1. Phosphate fertilizers; 2. Potash fertilizers; 3. Nitrogenous fertilizers. In addition to these, mixed fertilizers are used which may contain all three constituents.

Combined methods exist for the estimation of phosphoric acid, potash and nitrogen. These will be described first of all.

### (a) Phosphoric Acid.

Phosphoric acid may be determined gravimetrically or volumetrically. The gravimetric methods are the molybdate and citrate methods. In both the phosphoric acid is determined finally as magnesium pyrophosphate. It is determined volumetrically by titration with uranium acetate.

(a) Molybdate method. Separation from all other bases is accomplished by use of ammonium molybdate, whereby all phosphoric acid is precipitated in the form of a compound of varying composition. Phosphoric acid is determined from this.

To do this, 200 c.c. molybdate solution are added to a solution containing phosphoric acid (not exceeding .2 gr.  $P_2O_5$ ), which is then kept for 15–20 minutes at a temperature of 70–80° C. After standing three hours the supernatant liquid is filtered off, and the precipitate, as much as possible of which is allowed to remain in the beaker, is washed with a 15 per cent. solution of ammonium nitrate, containing 10 c.c. nitric acid to the liter. The washings are thrown on the same filter. The beaker, holding the main portion of precipitate, is placed under the funnel. A warm 2½ per cent. ammonia solution is poured on the filter in just sufficient amount to dissolve the precipitate upon it. It is then washed with cold ammonia of the same strength until a red coloration (molybdate reaction) no longer appears on adding ferrocyanide of potassium to a drop of the filtrate placed on a porcelain plate. The quantity

of ammonia used (150 c.c.) should just about suffice to dissolve the precipitate in the beaker on shaking. If not, more ammonia is added, and a clear solution is obtained. To this, for every 1 gr.  $P_2O_5$ , 10 c. c. magnesium mixture are added, drop by drop. It is stirred for some time without touching the sides of the beaker, and is filtered after at least three hours' standing. The precipitate is washed with  $2\frac{1}{2}$  per cent. ammonia until a portion of the filtrate, acidified with nitric acid, opalesces but slightly. Further manipulation is conducted in the usual manner.

Reagents used are prepared as follows :

*Molybdate solution* : 150 grams crystallized ammonium molybdate and 400 grams ammonium nitrate are dissolved in a liter of water, and the solution is poured into an equal volume of nitric acid (sp. gr. 1.19). The solution should be kept in the dark.

*Magnesium mixture* : 100 grams magnesium chloride and 140 grams ammonium chloride are dissolved in 1300 c.c. water, and diluted to two liters with 24 per cent. ammonia. It is filtered after standing in a stoppered flask for several days.

(β) Citrate method. By use of this method the precipitation of phosphates of lime, iron, etc., by ammonia is prevented by citric acid.

A quantity of solution containing phosphoric acid (not exceeding .2 gr.  $P_2O_5$ ) is treated with 100 c.c. citrate solution (prepared by dissolving 150 grs. citric acid in water, adding 500 c.c. 24 per cent. ammonia, and diluting to 1500 c.c.). If necessary, more ammonia is added, whereby turbidity must not ensue. The excess is neutralized with a few drops of nitric acid, and 25 c.c. magnesium mixture are added. The precipitate is treated as under (α).

The method is easily carried out and is much used. Since on the one hand some magnesium ammonium phosphate is dissolved by the excess of citric acid, and, on the other hand, small quantities of phosphate of lime, etc., are precipitated, the errors are balanced.

(γ) Uranium method. This method, which is considered as universally known, can only be used to determine water-soluble phosphoric acid. It is now rarely used, at any rate.

#### (b) Potassium Oxide.

This is determined as the double salt  $2KCl \cdot PtCl_4$  by using platinic chloride. It is only necessary that nothing but chlorides be

present, of which those of sodium, calcium and magnesium form platinum salts, soluble in alcohol, whereas that of potassium chloride is insoluble.

Should there be sulphates present, as is usually the case, they are converted into chlorides by adding a boiling chloride of barium solution (avoiding excess as much as possible) to the liquid, to which 1 c.c. hydrochloric acid has been added, without regarding a possible residue. The filtrate, or an aliquot portion of the same, is evaporated down to about 15 c.c. bulk, and sufficient platinic chloride is added to convert all salts present into double salts (1 gr. platinum to .5 gr. substance). It is stirred with a glass rod, evaporated to about 10 c.c., and 90 per cent. alcohol is added. After stirring for a while, and permitting to stand, it is filtered on a filter, moistened with alcohol, and washed with alcohol until the washings have become colorless.

The precipitate may be dried at 130° and weighed. But since it can contain small quantities of chlorides insoluble in alcohol, it is better to incinerate, filter and place contents in a porcelain crucible, and to ignite the residue separately with small quantities of pure oxalic acid at a high temperature.

#### (c) Nitrogen.

Nitrogen can be present as ammonia (ammonium salts), as nitrates, or as organic nitrogenous compounds. It may finally be present as a combination of two or three of these forms.

(a) Nitrogen as ammonia. The estimation is carried out by heating with caustic soda and absorbing the ammonia evolved in standardized acid. The operation is well known. When nitrogenous organic matter is simultaneously present, which is partially decomposed by boiling caustic soda with formation of ammonia, soda-lime or freshly calcined magnesia is used.

(β) Nitrogen as nitrates is estimated in an eudiometer graduated into tenths, as nitric oxide, which is caught up after liberation from the nitric acid, which is reduced with ferrous chloride (method of Schulze-Tiemann or Schlösing-Wagner).

(γ) Organic nitrogen. Various methods proposed for this estimation have been replaced by the method of Kjeldahl, the modified form of which, by Wilfarth, will be described here. 1-2 grs. substance are covered with 20 c.c. conc. sulphuric acid in a long-

necked, round-bottom flask of about 150 c.c. capacity. .7 gr. freshly prepared yellow mercuric oxide (or .5 gr. mercury) is added, and the whole is heated on a wire gauze, at first moderately, and finally to a brisk boiling. It is better to fasten the flask in a clamp in an inclined position in order to avoid loss by sputtering, and also to avoid the direct heating of the frequently uneven bottom of the flask.

The liquid is heated until colorless. It is allowed to cool and is poured into an Erlenmeyer flask of about  $\frac{3}{4}$  liter capacity, containing some water, and is then thoroughly rinsed out. After cooling, an excess\* of about 30 per cent. caustic soda is added, together with 25 c.c. of a 10 per cent. potassium sulphide solution. The latter precipitates all the mercury in the form of mercuric sulphide and simultaneously decomposes the mercury amides, from which the ammonia is expelled very slowly by alkalies. A few pieces of granulated zinc are added, to prevent bumping on distillation.

By distilling, all the ammonia is volatilized and is collected in a receiver containing 20 c.c. of half-normal sulphuric acid and 50 c.c. of water. The excess of acid is titrated and the nitrogen is calculated ( $1\text{H}_2\text{SO}_4$  is equivalent to 2N). In order to prevent alkali from being carried over, different forms of apparatus have been proposed. As a rule, a bulb tube is placed in the flask and connected with a condenser. Distillation is finished at the end of from 20–30 minutes. The contents of the flask usually heat up considerably, but a loss of ammonia is not to be feared, even when not cooled.

The most important fertilizers belonging to each of the three groups will now be described.

### 1. Phosphate Fertilizers.

They may be divided into :

<i>A. Phosphates containing water-insoluble phosphoric acid.</i>	<i>B. Phosphates containing water-soluble phosphoric acid.</i>
(a). Crude phosphates.	(b). Artificially-prepared phosphates.
Mineral phosphates.	Superphosphates.
Bone phosphates.	
Guano phosphates.	

\* The amount necessary is easily calculated approximately from the sulphuric acid used.

**A. Phosphates Containing Water-Insoluble Phosphoric Acid.**

Contain phosphoric acid principally in form of tricalcium phosphate, which, together with iron and aluminium present, is very slowly soluble.

In order to determine phosphoric acid in crude phosphates of sub-group (*a*)—phosphorite, apatite, bone meal, animal charcoal and Baker guano, 5 grs. substance, finely powdered, are boiled with 20 c.c. conc. nitric acid and 50 c.c. conc. sulphuric acid for  $\frac{1}{2}$  hour, and the solution, plus residue, is poured into a  $\frac{1}{2}$ -liter graduated flask, diluted to the mark and thoroughly agitated, after which it is filtered through a dry ribbed filter. In 50 c.c. of the filtrate the phosphoric acid is determined by the molybdate method.

Should the citrate method be preferred, however, the substance is dissolved in 30 c.c. concentrated sulphuric acid, instead of the above mixture. The remaining operation is conducted as in  $\beta$  (p. 73).

A nitrogen determination, according to Kjeldahl, as well as the detection of less valuable phosphates, is usually undertaken in bone-dust. The latter is detected by a high percentage of matter insoluble in hydrochloric acid (sand) and presence of ferric oxide and alumina.

Thomas slag is the most important product of the phosphate slags in sub-group (*b*). To determine the phosphoric acid in this, 10 grs. powdered material are moistened with water, and stirred with 5 c.c. of a mixture of equal parts sulphuric acid and water. As soon as the mass begins to harden, 50 c.c. concentrated sulphuric acid are added, and the whole is heated for  $\frac{1}{2}$ -hour on a sand-bath until white vapors arise. Meanwhile the mass is continually stirred. After cooling, it is carefully diluted with water, washed into a  $\frac{1}{2}$ -liter flask, diluted to the mark, well mixed, and allowed to stand several hours, in order to allow gypsum to separate. It is then filtered through a dry ribbed filter, and the phosphoric acid is determined in 50 c.c. filtrate by the citrate method.

**B. Phosphates Containing Water-Soluble Phosphoric Acid.**

To these belong principally the superphosphates obtained by dissolving crude phosphates in sulphuric acid, and which contain the monocalcium phosphate  $\text{CaH}_4(\text{PO}_4)_2$ , which is soluble in water.

Since the decomposition, however, is never perfect, there are present, beside these, di- and tricalcium phosphate, the quantity of which increases on standing for a long time, due to the action of aluminium and iron compounds present. The latter process is termed phosphoric acid reversion.

The phosphoric acid in commercial phosphates is, therefore, present in three forms:

(a) Monocalcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ . This is soluble in water, and, together with free phosphoric acid, is estimated as water-soluble phosphoric acid.

(b) Dicalcium phosphate,  $\text{CaHPO}_4$ . This is insoluble in water, but is, on the contrary, soluble in ammonium citrate. At times it is determined, together with the phosphoric acid present in form of iron or aluminium phosphate, as "citrate-soluble" or "reverted" phosphoric acid.

(c) Tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is insoluble in water and ammonium citrate. The phosphoric acid corresponding to this is designated as insoluble phosphoric acid.

(a) Estimation of water-soluble phosphoric acid.

Twenty grams of superphosphate are placed in a liter flask,\* and thoroughly agitated for  $\frac{1}{2}$  hour with 800 c.c. water. The liquid is then diluted to the mark, well mixed, filtered through a dry ribbed filter, and the phosphate is determined by the citrate method in 50 c.c. filtrate.

(b) Estimation of total phosphoric acid.

Five grams of superphosphate are suspended in 20 c.c. water, and then boiled with 100 c.c. concentrated nitric acid for  $\frac{1}{2}$  hour. The mixture is washed into a  $\frac{1}{2}$ -liter flask, diluted to the mark, filtered through a dry ribbed filter, and the phosphoric acid is determined in 50 c.c. filtrate by the molybdate method. The estimation of citrate-soluble phosphoric acid, concerning the value of which views differ, will not be further described.

## 2. Potassium Fertilizers.

The main source of these is the discarded Stassfurter salts, which consist chiefly of potassium and magnesium salts. The most important are Sylvite,  $5\text{KCl} + \text{NaCl}$ ; Carnallite,  $\text{KCl} + \text{MgCl}_2 +$

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\* Agitators worked by hand or water-power are very convenient.

$6\text{H}_2\text{O}$ ; Kainite,  $\text{KCl} + \text{MgSO}_4 + 3\text{H}_2\text{O}$ ; and Schönite,  $\text{K}_2\text{SO}_4 + \text{MgSO}_4 + 6\text{H}_2\text{O}$ .

In these the per cent. of potassium oxide is usually determined by one of the methods mentioned (p. 73).

### 3. Nitrogenous Fertilizers.

According to the division previously given, there belong in this group ammonium sulphate, potassium and sodium nitrates or a mixture of both (with an average percentage of nitrogen equalling 14.5-16 per cent.), dried-blood powder (12-15 per cent. N, about 1 per cent.  $\text{P}_2\text{O}_5$ ), horn meal (7-14 per cent. N, 5-6 per cent.  $\text{P}_2\text{O}_5$ ), powdered hide (6-10 per cent. N).

### 4. Mixed Fertilizers.

These are artificial mixtures of phosphorus, potassium and nitrogenous fertilizers, such as potassium-superphosphate, ammonium-superphosphate, saltpeter-superphosphate or natural products. To the latter belong Peru guano, dried-meat powder, fish-guano and dung.

Peru guano, formed from bird excrement and carcasses of marine animals, but less weathered than guano phosphate, contains, on the average, 8-11 per cent. nitrogen and 10-20 per cent. phosphoric acid.

Dried meat powder, made out of meat and bones of dead animals, contains 6-7 per cent. nitrogen and 10-15 per cent. phosphoric acid. Fish guano, made out of fish refuse, contains 5-12 per cent. N, 13-16 per cent.  $\text{P}_2\text{O}_5$ .

Dung, the mixture of solid and fluid excrement of cattle, horses, sheep, swine, together with litter, contains all three plant-nourishers in varying amounts. They may be confined within the following limits: Potassia, .40-.67 per cent.; phosphoric acid, .16-.28 per cent., and nitrogen, .34-.83 per cent.

## VI. Sugar Industry.

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THE investigation of sugar and saccharine products, such as beets, thin juice, molasses, etc., extends as a rule to the estimation of cane sugar, invert sugar, water, alkalinity, ash, and sometimes color.

Concerning the methods employed for this purpose the following may be said :

(a) Cane sugar. This may be determined from the specific gravity or by polarization.

(a) Specific gravity. Only in pure sugar solutions can sugar be estimated by means of specific gravity. Should other substances be in solution, they effect the specific gravity in different ways. In such solutions only an apparent value (for dry substance) expressed in per cent. of sugar, can be obtained.

The determination of specific gravity is conducted either with one of the usual forms of applicable apparatus, such as densimeter, pyknometer, hydrostatic balance, in which cases the percentage of sugar corresponding to the specific gravity must be referred to in a corresponding table, or by means of an areometer specially constructed for the purpose, the saccharometer of Balling or Brix. On account of its graduation direct sugar percentage readings can be made. In this case it is advantageous to use such saccharometers on which the scale is extended over a set of several consecutive spindles, and on which tenths per cent. can be easily read.

When the saccharometers are used to read volume percentage, an error, provided for on the instrument, due to change in volume by temperature, is taken into account.

Pyknometers and hydrostatic balance are then used when only small quantities of substance are obtainable.

(β) Polarization. It is taken for granted that the principle on which these instruments rest, as well as the arrangement of the same, is known. Recently the apparatus of Soleil-Ventzke-Scheib-

ler and the half-shadow apparatus of Schmidt and Haensch, have come into use. The former is adjusted for a transition color, a pale bluish violet, the latter for an even, faint shadow on both halves. The normal weight for both forms equals 26.048 grams; that is, a solution of 26.048 grs. pure cane sugar in 100 c.c. in a tube 200 mm. in length causes a rotation of 100°, or 1° corresponds with .26048 gr. sugar in 100 c.c. With the use of this normal weight and normal tube (200 mm.) the per cent. of sugar can consequently be read off directly. When a 100 mm. or 400 mm. tube is used, the degrees are to be doubled or halved.

Polarization is always preceded by clarification and decolorization with a solution of lead acetate (basic lead acetate). Cane sugar is dextro-rotary (+); invert sugar lævo-rotary (-).

(b) Invert sugar possesses the property of reducing Fehling's solution (see Reagents, p. 90) with separation of suboxide of copper. On the basis of this precipitated suboxide, which is reduced to metallic copper, the amount is determined by a method described later. The results obtained by polarization are influenced by the lævo-rotary power of invert sugar. Therefore, in the presence of the latter a different procedure, that of Clerget,\* is followed in the estimation of cane sugar. The description of this is given further on.

Syrup, molasses, etc., frequently contain invert sugar.

(c) Water. The use of small, flat-bottomed porcelain or enamelled sheet-iron capsules is advisable for fluid or semi-fluid products. Drying is done on a water-bath or in an air bath at 80–90° to begin with. Further drying should take place at 105° under the influence of a current of dry air, in order to expel the last traces of water. Stammer recommends the use of a special apparatus for this purpose. In the absence of the latter an ordinary air-bath is made to answer.

It is also recommended to mix the substance with a glass rod (4–5 grs. molasses, 8–10 grs. syrup and dense juices) with 20 grs. ignited quartz sand, free from dust, in a small porcelain capsule. This is then weighed and placed in an air-bath at 100° for  $\frac{1}{4}$  hour. It is then thoroughly stirred with a rod until a homogeneous mass is obtained and dried in an air-bath to constant weight.

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\* The same method is also made use of in the presence of raffinose.

(d) Alkalinity. This is influenced by the presence of free alkali, lime and free ammonia in the saccharine substance.

It is estimated by titration with normal or one-tenth normal acid, usually nitric acid, and is calculated into per cent. lime.

The indicator used is usually neutral, bluish-violet litmus tincture, which is added to the liquid. But in using deeply-colored substances, such as molasses, the indicator is not added, but instead, after each addition of acid the liquid is tested with a strip of bluish-violet, sensitive litmus paper.

(e) Ash. The residue left on ignition of a sugar, including the mechanically admixed impurities in the same, is called the "ash." The residue of a sugar free or freed from these impurities is called the "salts." The latter consists mainly of alkali sulphates or chlorides and carbonates arising from alkali salts of organic acids. Potassium predominates in these alkalies. Sometimes calcium carbonate, arising from soluble organic calcium salts, is found. These salts hinder crystallization of a part of the sugar and consequently cause a loss in the yield; and furthermore, even though this no longer holds good under the present conditions, one part salts is calculated to yield a decrease of five parts sugar. The complete ignition of a sugar is hard to accomplish by combustion, since the easily fusible alkali salts withhold small particles of carbon from combustion. Too strong a heat should likewise be avoided on account of possible volatilization of alkali chlorides. The incineration is therefore conducted as follows: The weighed sugar is charred in a spacious platinum dish until gas is no longer evolved. The coke is then moistened with water and crushed to a paste with a pestle. After the addition of a little hot water, heating and filtering, the residue on a small filter is repeatedly washed with hot water, and the filter and residue together are incinerated in the platinum dish. The filtrate added to this is evaporated to dryness on a water-bath, moistened with ammonium carbonate, dried at  $100^{\circ}$  and moderately ignited. The clean white residue is weighed.

In this manner the "ash" (carbonate ash) is ascertained. If the estimation of "salts" also be desired, a weighed quantity of sugar is dissolved in water (about 25 grs. sugar in 250 c.c.). The turbid solution is filtered, a portion of the filtrate is evaporated in a platinum dish, charred and heated as before.

Much simpler and quicker is the method of Scheibler. 3-5 grs. sugar are moistened with sulphuric acid in a platinum dish. After a few minutes the sugar blackens and decomposes. It is then heated over a very large flame, whereby thorough charring takes place with much swelling, hissing and gas evolution. To completely burn off the remaining coke the dish is placed in a muffle.

The action of the sulphuric acid converts the salts into sulphates, the weight of which is naturally higher than that of the salts originally present. The increase of weight equals almost exactly 10 per cent., by which the amount found must be decreased. The remainder is designated as sulphate ash.

(f) Color. The Stammer Colorimeter is used for this purpose; however, the determination is rarely carried out. The crude and refined products of the sugar industry which are subject to investigation are beets, beet juice, weak juice, dense juice, filling material, green syrup, molasses, osmosis fluid and cane sugar.

### 1. Beets.

The former assumption, that the sugar content in the juice of the beet bears a fairly constant relation to that of the beets (about 1 : .95), has been recently proven erroneous for different reasons, and therefore methods have been found for the direct determination of sugar in the beet. The "extraction" and "digestion" methods are recommended for this purpose.

(a) Extraction method (Scheibler). An exceedingly fine paste is prepared by rasping a cross section of the beet sample, by hand or machine. 35-40 grs. of this are weighed as quickly as possible on a tared pan and placed in the cylinder of a Soxhlet extractor. In the wide neck, 100 c.c. flask, with which the apparatus is provided, 75 c.c. of absolute alcohol are placed. The residue on the pan is rinsed into the cylinder with absolute alcohol, and then sufficient of the latter is added to fill the cylinder almost to the top of its siphon. The flask is attached to the apparatus and heated until extraction is complete. This as a rule is the case after 3-4 hours, in which time the alcohol will be siphoned 80-90 times. The water-bath is withdrawn, the flask is allowed to cool, and a sufficient quantity of lead acetate, 5-10 c.c., is added. It is then diluted to the mark, well mixed and polarized in a 200 mm. tube.

The rotation observed, multiplied by .26048, gives the amount of sugar contained in the weighed paste. If 26.048 grams of beets are used, then direct percentages of sugar are obtained.

(b) Digestion method (Rapp and Degner). Like the former, this depends on an alcohol extraction, the difference being that 52.1 grs., double the normal weight which is used, are directly placed in a graduated flask of exactly 200 c.c. capacity. The flask is marked down low and is provided with a widened neck into which a condenser, about 50 cm. in length and 10 mm. diameter, can be ground or securely fastened with a tight-fitting cork. Charging in is done with a glass rod, and the particles adhering to this, to the pan and to the neck of the flask, are washed in with a wash-bottle containing 90-92 per cent. alcohol. The flask is filled to four-fifths its capacity with the same alcohol. After adjusting the condenser, the flask is placed in an inclined position on a water-bath already heated to boiling, and the contents of the former are kept in ebullition for 15-20 minutes. The sugar is thereby completely dissolved in the liquid. The flask is removed, the condenser washed with alcohol and filled about 1 c.c. above the mark, without cooling. By successive immersions into the hot water-bath, to a point where ebullition begins, a thorough mixture is obtained. It is thereupon allowed to cool in the air for  $\frac{1}{2}$ - $\frac{3}{4}$  hour, and is finally brought to the temperature of the room by immersing in water. To the liquid, which has sunk down below the mark, 10-15 drops of lead acetate are added. It is then diluted to the mark with alcohol, well mixed by shaking, filtered and polarized. The readings made with the use of a 200 mm. tube yield direct sugar percentage. In order to compensate for the extracted pulp left in the flask, the result obtained is multiplied by .994. The true percentage is thus obtained. Stammer has in so far modified the operation as to cover an unlimited, usually much larger quantity of the paste with strong alcohol, and to dilute to such a volume that direct percentage of sugar in the beet can be read off in the polariscope after the sugar has become uniformly admixed. The operation requires particularly fine pulping of the beet paste in a beet cutting machine. This can only be accomplished in specially fitted laboratories.

**2. Beet Juice, Thin Juice.**

(a) Specific gravity. The estimation is made, as in one of the previously mentioned methods, preferably with Balling's saccharometer, in which case the corresponding specific gravity is referred to in the tables. The temperature required is  $17.5^{\circ}$ .

(b) Sugar. 100 c.c. juice are as accurately as possible placed in a flask provided with a second mark at 110 c.c. It is filled to the latter with lead acetate and is frequently shaken. Clarification and decolorization are effected completely after a few moments. In special cases where this quantity of lead acetate does not suffice, correspondingly more, about one-fifth volume of lead acetate, must be added. It is then filtered and polarized in a 200 mm. tube. The angle read off is increased by one-tenth, because of the dilution with lead acetate, and is then multiplied by .26048. The volume percentage—that is the grams sugar in 100 c.c.—is then obtained. Should the per cent. by weight be desired, it is only necessary to divide the first result by the specific gravity obtained, according to (a). Any bubbles which arise in pouring in the juice, and which are difficult to remove, are preferably depressed by the addition of a few drops of ether. Adhering liquid on the sides of the neck above the mark is removed with a roll of filter paper.

**3. Raw Sugar, Filling Material, Green Syrup, Molasses.**

(a) Sugar. Qualitative tests must be made for invert sugar prior to the sugar estimation. This is done by clarifying 20 grs. substance, dissolved in water, with lead acetate and diluting to 100 c.c. 50 cc. clear filtrate are mixed with 50 c.c. Fehling's solution (see Reagents, p. 90), heated on a wire gauze and kept boiling for 2 minutes. Should there be no suboxide of copper formed, or at most an inappreciable amount, the presence of invert sugar is not taken into account and the estimation proceeds as in (a). Should appreciable quantities of invert sugar be present, the estimation proceeds as in (β).

(a) Invert sugar is not present. The normal weight is dissolved in a 100 c.c. graduated flask and treated with 2-3 c.c. lead acetate and 1-2 c.c. alum solution. It is diluted to the mark, thoroughly shaken, and filtered. The clear liquid is polarized in a 200 mm. tube. This gives the percentage of saccharose.

Alumina in form of a thin hydrate paste is substituted for lead acetate, when purer sugars are used. (See Reagent, p. 90.) When lead acetate is used the alkaline reaction may be neutralized and the slight turbidity destroyed in the filtrate by introducing a glass rod moistened with conc. acetic acid.

(β) Invert sugar is present. The operation of Clerget is used, especially in the case of molasses.

Half the normal weight (13.024 grs.) is dissolved, with addition of 75 c.c. water, in a 100 c.c. flask. 5 c.c. hydrochloric acid sp. gr. 1.188 are added. The flask is warmed to 67–70° in a water-bath heated slightly above 70°. This requires 2–3 minutes. It is then kept, while shaking, as near 69° as possible for 5 minutes. It is quickly cooled, filled to the mark, and bone black—or, better, blood charcoal—is added, when necessary to decolorize. It is allowed to stand for a few minutes and is then polarized as near 20° as possible. The result is doubled when a 200 mm. tube is used. After the sugar has been inverted the liquid shows a strong laevo-rotary power (–I°).

In addition to this determination, polarization (α) is carried out in the usual manner (+ P°).

If S equal the sum of the angle before and after the inversion (omitting the negative sign of the invert sugar), therefore  $P + I^\circ$ , and  $t^\circ$  the temperature in centigrade degrees, taken at the time of reading, then the cane sugar R can be calculated from the formula :

$$R = \frac{100 S}{142.66 - \frac{1}{2} t^\circ}$$

This formula is based on the fact that pure saccharose, which rotates 100° before inversion, shows after inversion a rotation of  $42.66 - \frac{t^\circ}{2}$ . Therefore, the decrease of rotation of pure saccharose =  $142.66 - \frac{t^\circ}{2}$ .

(β) Invert sugar. When the presence of the latter is detected according to (α), the approximate amount is next ascertained. 10 grs. substance, dissolved in water, are clarified with lead acetate and diluted to 100 c.c. 10, 8, 6, 4 and 2 c.c. are placed in separate test tubes, 5 c.c. Fehling's solution are added to each, and

the contents are then boiled. Notice is now taken of the tube, whose contents are nearly decolorized. Should this be the case with the one containing 10 c.c., there is *less* than 1.5 per cent. invert sugar present, and the determination proceeds according to the method of Herzfeld. In the other case the method of Meissl and Hiller is used. For the latter method the number of c.c. in that test tube which is nearly decolorized give simultaneously the number of grams which, dissolved in 50 c.c., are used in the determination.

Every c.c. sugar solution (10 grs. to 100 c.c.) corresponds to .1 gr. substance. But in the method of Meissl and Hiller ten times the amount of Fehling's solution (50 c.c.) is used. Therefore, ten times the quantity of sugar is also taken. Consequently, every c.c. solution in the test represents 1 gr. substance in the latter determination.

Should the test therefore show that decolorization took place with 8 c.c., but that with 6 c.c. a blue tint remained, then 6 grs. dissolved in 50 c.c. are used.

(a) Method of Herzfeld. A solution, clarified with lead acetate, containing the normal weight in 100 c.c., is used. This is precipitated with sodium carbonate when any great excess of lead acetate has been used or when the sample is rich in alkaline earths.

When precipitation with soda is unnecessary 38.4 c.c. filtered solution diluted to 50 c.c. (= 10 grs. substance) are used.

When previous precipitation is necessary, 46.07 c.c. solution, increased to 60 c.c. with conc. soda solution, are withdrawn and filtered. 50 c.c. filtrate are then taken, and these also correspond to 10 grs. original substance. The 50 c.c. are placed in a dish or an Erlenmeyer flask with 50 c.c. Fehling's solution, and are heated to boiling for 3-4 minutes over a wire gauze with a triple burner. That moment is accepted as the beginning of ebullition when bubbles arise from the side as well as from the bottom of the vessel. Boiling is continued for exactly two minutes with the small flame of a single burner. Thereupon the flask or dish is immediately removed from the flame, 100 c.c. cold water previously boiled are added, and the contents are rapidly filtered with the aid of a pump, on a weighed asbestos filter (Fig. 8). The precipitate is rapidly washed on the filter with the aid of a feather, and is washed subsequently

with 300-400 c.c. hot water. The water is replaced by about 20 c.c. alcohol, finally with ether, and the tube is dried in an air-bath at 120-130°. The portion of the tube containing the cuprous oxide on the filter is next heated to a low red heat to oxidize and destroy organic substances, and is then reduced by heating slowly in a current of hydrogen. Reduction is complete in a few minutes. It is allowed to cool in hydrogen and the water collected in the neck allowed to evaporate. It is then placed in a desiccator and weighed after fifteen minutes. The invert sugar is gotten from the amount of reduced copper by means of the tables (p. 89).

The following details are yet to be considered: The asbestos must be proof against alkalies and acids and should previously be ignited. It is then suspended in water, poured on the glass wool in the tube, and pressed with a glass rod having a flattened end, so that a thin but perfectly solid layer, which filters without use of pump, is formed. It is then washed with alcohol and ether, dried and weighed.

During filtration a short, thick funnel is loosely placed on the tube. While washing, however, the latter is replaced by a funnel attached tightly to the tube by means of a rubber stopper. The liquid in the tube should not be allowed to run off entirely. The hydrogen used in reducing must be free from arsenic. The tube is attached to the hydrogen generator by a glass tube in a tightly-fitting rubber stopper, and is inclined upwards somewhat.

Instead of an asbestos filter, filter paper washed with hydrofluoric acid may be used. In this case, likewise, 300-400 c.c. hot water are used in washing. It is then incinerated, placed in a Rose crucible, covered with the perforated lid and reduced in hydrogen. When the quantity of cuprous oxide does not exceed .1 gr. it may be converted into cupric oxide by ignition in a porcelain crucible, weighed as such, and calculated into metallic copper.

(β) Method of Meissl and Hiller. This is used when the

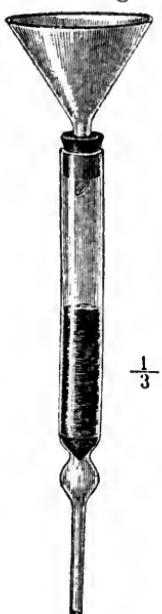


FIG. 8.  
Asbestos Filter.

amount of invert sugar exceeds 1.5 per cent. The necessary quantity of substance is ascertained from the previous experiments. In order to obtain this dissolved in 50 c.c., double the quantity is weighed out, brought to 100 c.c., after clarifying with lead acetate, and 50 c.c. of the filtrate are used. With this quantity the determination of invert sugar is conducted exactly as in the Herzfeld method.

In order to use the following tables of Meissl and Hiller the approximate ratio of saccharose to invert sugar (R : I) must be ascertained. The method of calculation is apparent from the following considerations: The invert sugar can be assumed to be equal to one-half the copper found. If p grs. substance were used and Cu grs. copper were found, then there were contained in p grs. substance approximately

$$\text{Cu} \quad \frac{\text{Cu}}{2}$$

$\frac{\text{Cu}}{2}$  grs. invert sugar. Therefore,  $\frac{2}{p} = i$  grs. invert sugar dissolved in 100 grs. substance. Furthermore, had the determination of cane sugar ( $\alpha \beta$  p. 85) given r per cent. cane sugar, then the total saccharine matter = r + i per cent. To determine the ratio of saccharine and invert sugar in 100 parts sugar, the invert sugar I is next calculated from the proportion (r + i) : i = 100 : I. From this  $I = \frac{100 \cdot i}{r + i}$ ; or, after substituting the values previously obtained:

$$I = \frac{\frac{100 \cdot 100}{2} \frac{\text{Cu}}{2}}{p \cdot r + 100 \frac{\text{Cu}}{2}}$$

The saccharose then becomes  $R = 100 - I$ . The ratio R : I is now known, and the factor corresponding to this ratio and to the amount of invert sugar approximately found is determined on the tables (p. 90). This factor F substituted in the equation  $I' = \frac{\text{Cu}}{p} F$  gives I' the true percentage of invert sugar.

(c) Water and ash are determined in the manner previously described. Sugar, water and ash added together and deducted from 100 yields the non-saccharine organic matter.

(d) Alkalinity. That which was previously stated answers in

general in this case. When molasses is used, 15-20 grs. are dissolved and diluted to 250 c.c. 25-50 c.c. of this solution are placed in a graduated cylinder and 1-2 c.c. litmus tincture are added. If the cylinder be held horizontally over a piece of white paper, a gray-green color is observed in the liquid when the molasses is alkaline. In this case another portion is titrated, as in the method already mentioned.

To distinguish whether a molasses is neutral, the contents of the cylinder are divided into two parts. To one part one drop normal acid is added, to the other a drop of normal alkali, whereupon the solutions, if originally neutral, should become either red or blue.

(e) Purity quotient is the sugar contained in 100 parts actual dry substance.

(f) "Rendement" or Yield is the number which designates how much crystallized cane sugar is capable of being obtained from a raw sugar. The customary calculation in practice fundamentally assumes 5 parts by weight; sugar is prevented from crystallizing by 1 part by weight of soluble salts. The "rendement" in Germany and England is therefore obtained by deducting five times the weight of salt content from the cane sugar content.

The assumption is a rather arbitrary one.

*Tables of Herzfeld.*

Copper. mg.	Invert Sugar. Per Cent.						
50	0.05	120	0.40	190	0.79	255	1.16
55	0.07	125	0.43	195	0.82	260	1.19
60	0.09	130	0.45	200	0.85	265	1.21
65	0.11	135	0.48	205	0.88	270	1.24
70	0.14	140	0.51	210	0.90	275	1.27
75	0.16	145	0.53	215	0.93	280	1.30
80	0.19	150	0.56	220	0.96	285	1.33
85	0.21	155	0.59	225	0.99	290	1.36
90	0.24	160	0.62	230	1.02	295	1.38
95	0.27	165	0.65	235	1.05	300	1.41
100	0.30	170	0.68	240	1.07	305	1.44
105	0.32	175	0.71	245	1.10	310	1.47
110	0.35	180	0.74	250	1.13	315	1.50
115	0.38	185	0.76				

*Tables of Hiller.*

R : I.	Cu <sub>2</sub> = 200 mg.	175 mg.	150 mg.	125 mg.	100 mg.	75 mg.	50 mg.
0 : 100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
10 : 90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
20 : 80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
30 : 70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
40 : 60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50 : 50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
60 : 40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
70 : 30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
80 : 20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
90 : 10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
91 : 9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
92 : 8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
93 : 7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
94 : 6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
95 : 5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
96 : 4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
97 : 3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
98 : 2	49.9	48.9	48.5	47.2	45.8	43.3	40.0
99 : 1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

## Reagents Used in the Methods Described.

1. Lead acetate. 600 grs. sugar of lead and 200 grs. litharge are covered with two liters of water and allowed to stand, with frequent agitation, for twelve hours in a warm place. The liquid is filtered from the sediment and placed in a reagent bottle. The latter is best provided with a double-bored stopper in which are adjusted a siphon and a soda-lime tube.

2. Alumina. Commercial aluminium chloride is dissolved in a flask in 100 volumes water and precipitated with ammonia to alkaline reaction. The precipitate of aluminium hydrate is allowed to settle, the supernatant liquid is drawn off, and the precipitate is washed by decantation until alkaline reaction ceases. The aluminium hydrate so prepared is preserved as a thick paste.

3. Fehling's solution. This consists of the two following solutions :

(a) 34.639 grs. crystallized copper sulphate are dissolved in 500 c.c. water.

(b) 173 grs. Seignette salt are dissolved in 400 c.c. water. 100 c.c. sodium hydrate solution containing 50 grs. caustic soda are

added, and the solution is filtered if necessary. The solutions are kept separate, and are mixed in equal volumes prior to every experiment.

#### 4. Press Cake.

*Sugar.* Portions from different parts of the press cake under investigation are selected, ground and mixed, and of this uniform stiff mass, so obtained, the normal weight is taken. This quantity is mixed with water, placed in a 200 c.c. flask filled to the mark with a little lead acetate and wash water, and the solution is polarized in a 400 mm. tube. The reading gives the percentage of sugar. The method is not absolutely exact, but suffices for technical purposes. If the volume occupied by the calcium carbonate be taken into consideration, 25 grs. may be taken instead of the normal weight, and the readings still considered as percentage.

#### 5. Lime Saccharate.

(a) *Sugar.* Half the usual weight is placed in a small mortar and ground with a little water to a uniform paste. A little phenol-phthalein is added as indicator, and conc. acetic acid is added while the particles are crushed, and the solution is stirred until the red color disappears. When the decomposition is complete the solution is washed into a 100 c.c. flask, a small amount of lead acetate is added, and the whole is diluted to the mark. It is then filtered and polarized. When a 200 mm. tube is used the reading is doubled, in order to obtain per cent. units.

(b) *Lime.* 2-5 grs. are weighed, ground in a mortar and titrated with normal or half-normal acid, using phenol-phthalein as an indicator. The result is expressed in lime units.

#### 6. Bone Black.

This substance serves as a decolorizer whose use in sugar factories is undoubtedly diminishing. The investigation includes water, carbon, sand, clay, carbonate of lime, sulphate of lime, calcium sulphide and phosphoric acid.

(a) *Water.* A weighed quantity, about 10 grs. sample, used in form of a coarse powder, is dried to constant weight at 140-150° in a well-ground, stoppered weighing-bottle.

(b) *Carbon, sand and clay.* For this purpose, as in the follow-

ing, the finely-powdered and air-dried bone black is used, and since the water is different in this sample from that in the former, a separate water determination is made. The results are reckoned as anhydrous bone black.

The operation is conducted as follows: 10 grs. substance are moistened with water. 50 c.c. hydrochloric acid are carefully added, and the mixture is heated to boiling for  $\frac{1}{4}$  hour. It is then filtered through a dried and weighed filter and washed with hot water until acidity ceases. The filtrate (*A*) is collected in a liter flask. The filter and residue are dried to constant weight. The increase in weight represents carbon + sand + clay. Filter and residue are now ignited. Sand and clay remain. The carbon is calculated from the difference between this and the former weight.

(c) Carbonate of lime. The Scheibler apparatus (Fig. 9) is almost exclusively used for this purpose.

The generation of carbonic acid takes place in flask *A*, in which the finely-powdered substance is placed and allowed to come in contact with the hydrochloric acid in the gutta-percha cylinder *S*. The carbonic acid evolved passes through the glass tube, which is sealed in the stopper, and then through the rubber tube *r* into a thin rubber balloon, *K*, contained in the flask *B*. Besides the connection with *A*, the flask *B* is connected, by means of the glass tube *uu*, with the graduated tube *C*, and finally with a third, which communicates with the outer air. This may be established or prevented by the pinchcock *q*.

The eudiometer *C*, divided into 25 c.c., communicates below with the tube *D*, whose lower end is provided with an exit tube which extends to the floor of the two-neck flask *E*. Pinchcock *p* is placed on a piece of rubber tubing between *D* and *E*. By forcing air into flask *E*, preferably with an elastic ball, the water present in *E* can be forced into *C* and *D*. On the other hand, by opening the pinchcock *p* it may be let out of *C* and *D* into *E*.

*Operation.*—The normal weight (1.7 grs.) required by the apparatus of the finely-powdered bone black is weighed out and placed in the thoroughly dried flask *A*. The gutta-percha vessel *S* is then filled with hydrochloric acid of 1.12 density (2 vols. conc. hydrochloric acid, 1 vol. water) and carefully placed, with forceps, in *A*, so that it rests on the glass side in a slanting position.

After raising the water in *C* to the zero mark by forcing air into the flask *E* and simultaneously opening the clip *p*, *A* is closed with the well-greased stopper.

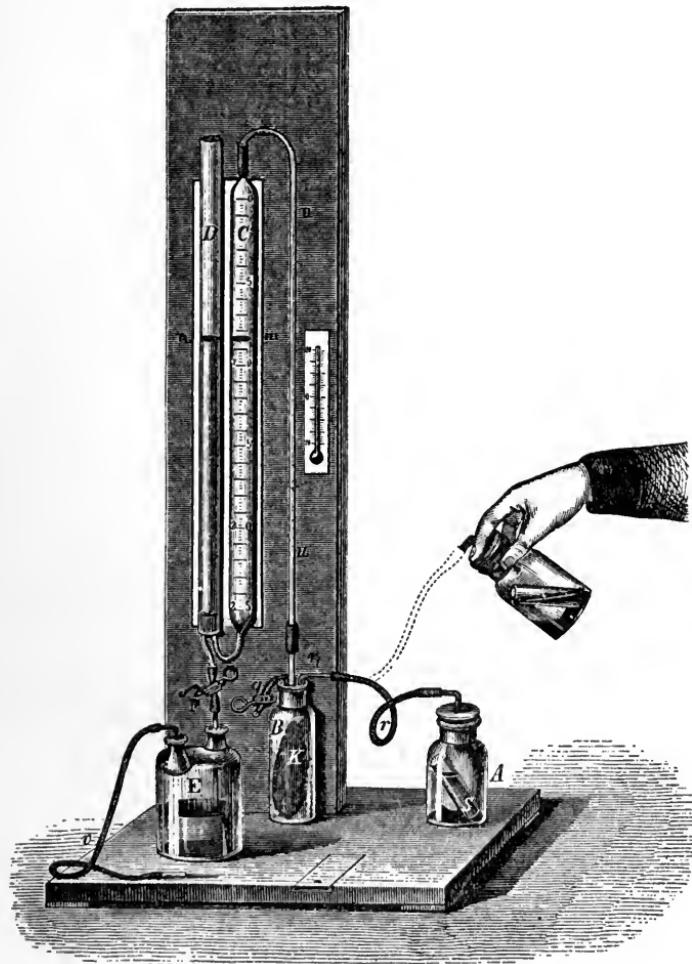


FIG. 9.—Scheibler's Apparatus.

Any air pressure and consequent change in the level of the liquid in *C* and *D* are removed by opening the clip *q* once. The vessel *A* is taken between thumb and middle finger of the right hand,

while the forefinger presses the stopper. The flask is then inclined sufficiently to allow the acid to escape from the gutta-percha holder. Decomposition, which ensues, is sustained and augmented by careful continued shaking of the flask *A*. Simultaneously the clip *p* is opened with the left hand, and as much water is allowed to flow into *E* as is necessary to bring both levels in tubes *C* and *D* to about the same height; that in *D* somewhat higher than in *C*.

When water in *C* ceases to descend on prolonged agitation of *A*, the decomposition is complete. 5-10 minutes are allowed to elapse in order to allow pressure and temperature to equalize, after which the levels in *C* and *D* are brought to the same height by carefully opening the clip *q*.

The level in *C* is read off, as well as the temperature of a thermometer placed in the apparatus. The direct percentage of carbonate of lime is found, by means of these two numbers, on the accompanying tables calculated by Scheibler.

(*d*) Sulphate of lime. 500 c.c. of the filtrate *A* (see *b*) are nearly neutralized with sodium carbonate, concentrated by evaporation and precipitated with barium chloride. The sulphuric acid obtained is calculated into calcium sulphate.

(*e*) Calcium sulphide. About 10 grs. finely-powdered bone black are dissolved in fuming nitric acid or hydrochloric acid and potassium chlorate. The liquid is filtered. The filtrate is diluted to 500 c.c., and the sulphuric acid in 250 c.c. is determined as before. The sulphuric acid found in (*d*), deducted from that just found, gives the sulphuric acid corresponding to the sulphur of the calcium sulphide, from which the latter is readily calculated.

(*f*) Phosphoric acid. This determination is minutely described in the chapter on Fertilizers. It is of special importance in bone-black waste.

## VII. Fermentation Industries.

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In this chapter the investigation of raw products containing starch, malt, yeast and spirits, will be discussed.

### 1. Raw Products Containing Starch.

The most important determinations required are starch and total nitrogen.

(a) Starch. Two methods are in use, in connection with the methods of solution used in practice. The one is conducted with high pressure, the other without. The starch, dissolved in either one or the other way, is eventually inverted and calculated from the dextrose formed.

(a) Method of Reinke, with use of high pressure. The finely-divided substance is used in form of a flour, in a separate portion of which the water has been determined. In addition, the water in the original substance must be ascertained. The values found for the flour are recalculated on this.

Three grs. flour are moistened in a metal or glass beaker with 25 c.c. 1 per cent. solution of lactic acid and 30 c.c. water. The mass is covered with a watch crystal and heated for  $2\frac{1}{2}$  hours at  $3\frac{1}{2}$  atmospheres in a Soxhlet steam-kettle, or, in the absence of the latter, in a Lintner pressure-flask. After cooling, 50 c.c. hot water are added. The solution is then placed in a 250 c.c. flask and diluted to the mark. After occasional shaking, during a period of a half hour's standing, the solution is filtered.

200 c.c. of the filtrate, to which 15 c.c. hydrochloric acid (sp. gr. 1.125) have been added, are briskly boiled on a reflux condenser for two hours. Upon cooling, the liquid is neutralized with caustic soda to faint acid reaction and diluted to 500 c.c. In order to know once and for all how much alkali to add, 15 c.c. hydrochloric acid (1.125) are titrated with the former. The quantity

*Determination of Grape-Sugar (Dextrose). F. Allihn.*

Copper, mg.	Dex- trose, mg.	Copper, mg.	Dex- trose, mg.	Copper, mg.	Dex- trose, mg.	Copper, mg.	Dex- trose, mg.	Copper, mg.	Dextrose, mg.
10	6.1	56	28.8	102	51.9	148	75.5	194	99.4
11	6.6	57	29.3	103	52.4	149	76.0	195	100.0
12	7.1	58	29.8	104	52.9	150	76.5	196	100.5
13	7.6	59	30.3	105	53.5	151	77.0	197	101.0
14	8.1	60	30.8	106	54.0	152	77.5	198	101.5
15	8.6	61	31.3	107	54.5	153	78.1	199	102.0
16	9.0	62	31.8	108	55.0	154	78.6	200	102.6
17	9.5	63	32.3	109	55.5	155	79.1	201	103.2
18	10.0	64	32.8	110	56.0	156	79.6	202	103.7
19	10.5	65	33.3	111	56.5	157	80.1	203	104.2
20	11.0	66	33.8	112	57.0	158	80.7	204	104.7
21	11.5	67	34.3	113	57.5	159	81.2	205	105.3
22	12.0	68	34.8	114	58.0	160	81.7	206	105.8
23	12.5	69	35.3	115	58.6	161	82.2	207	106.3
24	13.0	70	35.8	116	59.1	162	82.7	208	106.8
25	13.5	71	36.3	117	59.6	163	83.3	209	107.4
26	14.0	72	36.8	118	60.1	164	83.8	210	107.9
27	14.5	73	37.3	119	60.6	165	84.3	211	108.4
28	15.0	74	37.8	120	61.1	166	84.8	212	109.0
29	15.5	75	38.3	121	61.6	167	85.3	213	109.5
30	16.0	76	38.8	122	62.1	168	85.9	214	110.0
31	16.5	77	39.3	123	62.6	169	86.4	215	110.6
32	17.0	78	39.8	124	63.1	170	86.9	216	111.1
33	17.5	79	40.3	125	63.7	171	87.4	217	111.6
34	18.0	80	40.8	126	64.2	172	87.9	218	112.1
35	18.5	81	41.3	127	64.7	173	88.5	219	112.7
36	18.9	82	41.8	128	65.2	174	89.0	220	113.2
37	19.4	83	42.3	129	65.7	175	89.5	221	113.7
38	19.9	84	42.8	130	66.2	176	90.0	222	114.3
39	20.4	85	43.4	131	66.7	177	90.5	223	114.8
40	20.9	86	43.9	132	67.2	178	91.1	224	115.3
41	21.4	87	44.4	133	67.7	179	91.6	225	115.9
42	21.9	88	44.9	134	68.2	180	92.1	226	116.4
43	22.4	89	45.4	135	68.8	181	92.6	227	116.9
44	22.9	90	45.9	136	69.3	182	93.1	228	117.4
45	23.4	91	46.4	137	69.8	183	93.7	229	118.0
46	23.9	92	46.9	138	70.3	184	94.2	230	118.5
47	24.4	93	47.4	139	70.8	185	94.7	231	119.0
48	24.9	94	47.9	140	71.3	186	95.2	232	119.6
49	25.4	95	48.4	141	71.8	187	95.7	233	120.1
50	25.9	96	48.9	142	72.3	188	96.3	234	120.7
51	26.4	97	49.4	143	72.9	189	96.8	235	121.2
52	26.9	98	49.9	144	73.4	190	97.3	236	121.7
53	27.4	99	50.4	145	73.9	191	97.8	237	122.3
54	27.9	100	50.9	146	74.4	192	98.4	238	122.8
55	28.4	101	51.4	147	74.9	193	98.9	239	123.4

added is then made less than that required to fully neutralize. The dextrose is determined with Fehling's solution in 50 c.c. of neu-

*Determination of Grape-Sugar (Dextrose). F. Allihn.—Continued.*

Copper. mg.	Dex- trose. mg.	Copper. mg.	Dex- trose. mg.	Copper. mg.	Dex- trose. mg.	Copper. mg.	Dex- trose. mg.	Copper. mg.	Dextrose. mg.
240	123.9	285	148.3	330	173.1	375	198.6	420	224.5
241	124.4	286	148.8	331	173.7	376	199.1	421	225.1
242	125.0	287	149.4	332	174.2	377	199.7	422	225.7
243	125.5	288	149.9	333	174.8	378	200.3	423	226.3
244	126.0	289	150.5	334	175.3	379	200.8	424	226.9
245	126.6	290	151.0	335	175.9	380	201.4	425	227.5
246	127.1	291	151.6	336	176.5	381	202.0	426	228.0
247	127.6	292	152.1	337	177.0	382	202.5	427	228.6
248	128.1	293	152.7	338	177.6	383	203.1	428	229.2
249	128.7	294	153.2	339	178.1	384	203.7	429	229.8
250	129.2	295	153.8	340	178.7	385	204.3	430	230.4
251	129.7	296	154.3	341	179.3	386	204.8	431	231.0
252	130.3	297	154.9	342	179.8	387	205.4	432	231.6
253	130.8	298	155.4	343	180.4	388	206.0	433	232.2
254	131.4	299	156.0	344	180.9	389	206.5	434	232.8
255	131.9	300	156.5	345	181.5	390	207.1	435	233.4
256	132.4	301	157.1	346	182.1	391	207.7	436	233.9
257	133.0	302	157.6	347	182.6	392	208.3	437	234.5
258	133.5	303	158.2	348	183.2	393	208.8	438	235.1
259	134.1	304	158.7	349	183.7	394	209.4	439	235.7
260	134.6	305	159.3	350	184.3	395	210.0	440	236.3
261	135.1	306	159.8	351	184.9	396	210.6	441	236.9
262	135.7	307	160.4	352	185.4	397	211.2	442	237.5
263	136.2	308	160.9	353	186.0	398	211.7	443	238.1
264	136.8	309	161.5	354	186.6	399	212.3	444	238.7
265	137.3	310	162.0	355	187.2	400	212.9	445	239.3
266	137.8	311	162.6	356	187.7	401	213.5	446	239.8
267	138.4	312	163.1	357	188.3	402	214.1	447	240.4
268	138.9	313	163.7	358	188.9	403	214.6	448	241.0
269	139.5	314	164.2	359	189.4	404	215.2	449	241.6
270	140.0	315	164.8	360	190.0	405	215.8	450	242.2
271	140.6	316	165.3	361	190.6	406	216.4	451	242.8
272	141.1	317	165.9	362	191.1	407	217.0	452	243.4
273	141.7	318	166.4	363	191.7	408	217.5	453	244.0
274	142.2	319	167.0	364	192.3	409	218.1	454	244.6
275	142.8	320	167.5	365	192.9	410	218.7	455	245.2
276	143.3	321	168.1	366	193.4	411	219.3	456	245.7
277	143.9	322	168.6	367	194.0	412	219.9	457	246.3
278	144.4	323	169.2	368	194.6	413	220.4	458	246.9
279	145.0	324	169.7	369	195.1	414	221.0	459	247.5
280	145.5	325	170.3	370	195.7	415	221.6	460	248.1
281	146.1	326	170.9	371	196.3	416	222.2	461	248.7
282	146.6	327	171.4	372	196.8	417	222.8	462	249.3
283	147.2	328	172.0	373	197.4	418	223.3	463	249.9
284	147.7	329	172.5	374	198.0	419	223.9		

tralized solution, corresponding to .24 gr. substance. For this purpose, according to Allihn, 30 c.c. copper sulphate solution and 30

c.c. alkaline Seignette solution are diluted in a porcelain dish of 200 c.c. capacity with sufficient water to bring the total volume, after adding the sugar solution under examination, to 145 c.c.—in this instance 35 c.c. This solution is boiled. 50 c.c. dextrose solution are run into the boiling liquid, which is held in ebullition for two minutes from the moment that boiling again sets in.

Further treatment is conducted in exactly the same manner as described in the determination of invert sugar. In the accompanying tables of Allihn are found the values for dextrose corresponding to the copper obtained. To calculate into starch, the quantity of dextrose is multiplied by .9.

The method is applied mainly to the determination of starch in potatoes.

(β) Method of Märcker, without the use of high pressure.

Solution of the starch is here accomplished by diastase. 3 grs. substance, previously extracted in a Soxhlet apparatus with ether, if necessary, to free from fat, are boiled with 100 c.c. water for  $\frac{1}{2}$  hour on a reflux condenser. The solution is cooled to 65° and 10 c.c. malt extract (prepared according to directions given below) are added. The solution is kept at 65° for  $\frac{1}{2}$  hour. Thereupon the solution is again boiled for  $\frac{1}{4}$  hour, again cooled to 65°, and allowed to remain at this temperature for  $\frac{1}{2}$  hour after addition of another 10 c.c. malt extract. Finally it is boiled, cooled, diluted to 200 c.c. and filtered. 200 c.c. filtrate are inverted with 15 c.c. hydrochloric acid (1.125), then neutralized and diluted to 500 c.c.

50 c.c. are reduced with Fehling's solution. The remaining operation is conducted precisely as in (a).

From the dextrose values found in the tables, that amount is to be deducted, which corresponds to 1.6 c.c. malt extract contained in 50 c.c. The difference multiplied by .9 gives the starch in .24 gr. flour.

*Preparation of malt extract.*—100 grs. bruised kiln-dried malt are covered with 1 L. water and macerated, with occasional agitation, for a period of 6 hours. It is thereupon filtered. The filtrate keeps better on addition of a little chloroform.

*Dextrose value of the malt extract.*—50 c.c. are diluted with 150 c.c. water and boiled on a reflux condenser in a flask with 15 c.c. hydrochloric acid (1.125) for two hours. It is then nearly neu-

tralized, diluted to 500 c.c., and 50 c.c. treated, as heretofore, with Fehling's solution. The dextrose value, corresponding to the copper found, multiplied by .32, gives the amount of dextrose corresponding to 1.6 c.c. malt extract, which is to be deducted.

(b) Total nitrogen. The determination is conducted according to the method of Kjeldahl, in precisely the same manner as under Nitrogen Fertilizers (p. 78). 1 gr. substance is used. By multiplying the nitrogen found by 6.25 the crude proteids are obtained.

## 2. Starch.

The investigation includes chiefly the determination of water, the detection of impurities and adulterants, as well as establishing the raw product from which it was made.

For the latter purpose use is made chiefly of the microscopic method of investigation, which, however, will not be further described here.\* A starch determination can be conducted by inverting 2.5-3 grs. substance by boiling with 200 c.c. water and 20 c.c. hydrochloric acid (1.125) for three hours. The dextrose formed is determined with Fehling's solution, as before. According to Sachsse, 100 grs. dextrose equal 91.67 grs. starch. The operation is seldom conducted.

(a) Water. About 10 grs. starch are weighed out, dried at first for an hour at 40-50°, and then for 3-4 hours to constant weight at 120° C.

(b) Impurities and adulterants. These may be both organic and inorganic in nature :

(a) Inorganic matter. This is ascertained from the amount of ash present, and is estimated by an ash determination. Mineral adulteration is usually done with sand, gypsum, chalk, heavy spar and clay.

(b) Organic. The starch is dissolved with malt extract and the residue is examined. It contains such organic impurities as wood particles, fibres, coal-dust, chaff, fungus spores, etc. Organic adulterants can hardly be else than cheaper grades of starch which are added to the finer, and which are determined microscopically.

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\* An excellent reference is the small book of V. Höhnel, "Starch and Ground Products."

### 3. Malt.

For this investigation the combined method of E. Jalowetz, prepared at the Congress of Agriculture and Forestry in Vienna, 1890, will be discussed.

(a) Water. 4-5 grs. malt are weighed off in form of whole grains and are bruised as nearly quantitatively as possible in a special mill. The substance, which is placed in watch crystals provided with clasps, is heated in an atmosphere of dry hydrogen in a drum-shaped water-bath. If the latter is inaccessible, it is dried in a well-ventilated air-bath at 98-104°. In the first case drying requires 6 hours; in the latter, 3-4 hours. It is finished when the loss in weight no longer exceeds .25 per cent.

Very moist malt is dried at 40-50°.

(b) Extract. 50 grs. whole malt are weighed out and ground, without loss, in a malt mill. It is then washed with about 200 c.c. water of 45° C. temperature, in a weighed beaker of about 500 c.c. capacity, and is kept in a water-bath at the same temperature for a half hour. The temperature of the bath is thereupon increased 1° from minute to minute, so that after a period of 25 minutes a temperature of 70° is reached. The mash is kept at this temperature until saccharizing is complete, which is usually the case in about  $\frac{1}{2}$  hour. The end reaction is ascertained by means of iodine tests which are calculated in this manner: A drop of mash is placed on a porcelain dish. A drop of iodine solution is added and allowed to stand for a while. The first test is made 10 minutes after saccharizing has begun; that is, after the mash has attained a temperature of 70°. Further tests are made at intervals of 5-10 minutes. Saccharizing is considered finished when the iodine tests show a weak red or a pure yellow color. The time consumed, up to this moment, is named the "time of saccharizing." The mash is now removed from the water-bath, cooled, and treated with approximately 200 c.c. cold water. On the balance, the weight of the mash is increased by addition of water to 450 grs. It is mixed and filtered into a dry flask through a ribbed filter. The filter should be capable of receiving the entire quantity of mash at once. The first portion of about 100 c.c. is replaced in the filter and the density of the subsequent filtrate is determined with a pyknometer. The latter, filled with the wort, should stand about one hour in a

bath at  $17.5^{\circ}$ . By means of the density, the corresponding extract e, that is, the extractive matter in 100 c.c., is sought for in Balling's tables.

The extract E of the air-dried malt is found by means of the formula  $(100 - e) : e = (400 + \frac{W}{2}) : \frac{E}{2}$  where W equals the amount of water expressed in per cent.

It then becomes:

$$E = 2 \cdot \frac{e(400 + \frac{W}{2})}{100 - e}.$$

In 100 parts by weight of wort there are e parts extract, and  $100 - E$  parts water. The total weight of the mash equaled 450 grs., i.e., 400 grs. water and 50 grs. malt, with  $W\%$  water, hence in all  $400 + \frac{W}{2}$  grs. water. If the percentage of extract in the malt equal E, then in 50 grs. malt there are contained  $\frac{E}{2}$  grs. extract. The previously constructed proportion is hereby sufficiently explained.

(c) Maltose. The estimation of maltose is conducted gravimetrically by reduction with Fehling's solution.

30 c.c. of the wort obtained as in (b) are diluted to 200 c.c. 25 c.c. of the dilute solution are run into 50 c.c. boiling Fehling's solution. It is kept boiling for 4 minutes, the suboxide of copper is filtered through an asbestos filter, and the remaining operation is conducted as heretofore. The maltose corresponding to the copper found is determined from the tables of Wein (see page 102).

Let the maltose be m, then the original 30 c.c. wort contain 8m grams maltose. Furthermore, if the extract in 100 grs. be e, then the extract in 30 c.c. or 30 d grs. ( $d = \text{density}$ ) = .3 . d . e. In order to find the maltose M in E grs. extract, use is made of the proportion:

$$.3 . d . e : 8m = E : M.$$

Therefore the percentage of maltose is

$$M = \frac{8m E}{.3 . d . e}.$$

(d) Diastatic value. The estimation depends on the fact that a malt extract of known value inverts more starch the higher its

*Wein's Tables for the Determination of Maltose.*

Copper, mg.	Maltose, mg.	Copper, mg.	Maltose, mg.
30	25.3	170	149.4
40	33.9	180	158.3
50	42.6	190	167.2
60	51.3	200	176.1
70	60.1	210	185.0
80	68.9	220	193.9
90	77.7	230	202.9
100	86.6	240	211.8
110	95.5	250	220.8
120	104.4	260	229.8
130	113.4	270	238.8
140	122.4	280	247.8
150	131.4	290	256.6
160	140.4	300	265.5

diastatic value. The determination is conducted with a normal starch and a malt extract.

*Starch solution.*—To prepare this, a soluble starch is used. The latter is prepared by adding sufficient 7½ per cent. hydrochloric acid to cover any desired quantity of prime potato starch. This is allowed to stand 7 days at ordinary temperature or 3 days at 40°. The acid is drawn off and the residue is washed with cold water by decantation until acidity ceases. It is then air dried. 2 grs. of this starch are dissolved in hot water. The solution will remain clear for a number of days, but can be used even after it has become turbid.

*Malt extract.*—25 grs. kiln-dried malt or crushed green malt are extracted with 500 c.c. water at ordinary temperature for 6 hours. It is then filtered. The solution is refiltered as long as the filtrate comes through turbid. When green malt is used, the filtrate is diluted with an equal volume of water before use.

*Experiment.*—Introduce 10 c.c. starch solution in each of 10 test-tubes. There is then added to each of these .1, .2—1 c.c. malt extract. They are well shaken and the diastase is allowed to act at the surrounding temperature for 1 hour. After this time has elapsed 5 c.c. Fehling's solution are added to each of the tubes, which are then well shaken and placed for 10 minutes in boiling water. The tube in which all the copper oxide is reduced is easily

recognized. In this one the liquid over the suboxide appears faintly blue, whereas in the next higher it is yellow, and in the next lower it is deep blue. In very exact determinations, another test is made between the two limits found by increasing the malt extract by .02 c.c. and observing similar conditions. The fermenting value of a malt is made equal to 100, according to Lintner, when .1 c.c. of the malt extract, prepared as above, just reduces 5 c.c. Fehling's solution. It is graded in the same proportions as the extract used increases, *i. e.*, .2 c.c. malt extract = 50; .5 c.c. malt extract = 20, etc. The fermentation values obtained are doubled when green malt, which is diluted with an equal volume of water, is used.

#### 4. Yeast.

*Determination of fermentation value.*—50 grs. yeast, together with 400 c.c. 10 per cent. cane sugar solution, are placed in a flask and closed with a rubber stopper, to which there is attached a small sulphuric acid drying apparatus. Flask, contents and drying apparatus are weighed and heated in a water-bath at exactly 30° C. After 24 hours the loss in weight, due to the evolution of carbonic acid, is determined.

According to Heyduck, compressed yeast free from starch, and of which 5 grs. are used for analysis, should yield 8-12 grs. carbonic acid. .4904 gr. carbonic acid corresponds to 1 gr. cane sugar decomposed.

#### 5. Spirits.

(a) Alcohol. When pure spirits are used, this can be determined by certain areometers and alcoholometers. For this purpose the officially adopted instruments are preferably used. The normal temperature is set at 12° R. in Austria and at 12 $\frac{4}{9}$ ° R. in Germany. Readings are made at any temperature, and from the apparent strength and the thermometer reading the true strength is interpolated by means of tables which accompany the instruments. The true volume of the spirits, on the basis of the true strength, may be determined, by the use of another table, from the apparent volume, at the prevailing temperature. A third table contains the numbers for calculation of the weight of spirit into true volume.

When impure spirits are examined, such as fermented mashes, this method is not suitable. The alcohol is in this case determined by

the method of distillation. For this purpose 100-200 c.c. liquid to be tested are placed in a flask with an equal volume of water and are distilled off exactly one-half. The distillate contains all the alcohol originally present in the same quantity of liquor as before distillation. The alcohol may be determined as heretofore by finding the density of the distillate with an alcoholometer or a pyknometer.

(b) Fusel oil. The most convenient methods are that of Rose and that of Traube (using stalagmometer). The latter is less reliable, but can be rapidly executed and is often sufficiently exact.

(a) Method of Rose (modified by Stutzer and Reitmair). This depends on the following principle: On shaking a mixture of ethyl alcohol and water with chloroform, a certain portion of the former dissolves in the chloroform, which thereby experiences an increase in volume. When the alcohol contains fusel oil this is also dissolved. Therefore a greater increase of volume takes place. The amount of this latter increase affords a means of establishing the quantity of fusel oil.

The agitator used consists of a glass tube, sealed at one end, while the other possesses a pear-shaped enlargement, provided with a tightly fitting stopper. The middle of the tube is contracted and graduated. There are two different sizes of this apparatus. In the smaller form of Herzfeld the graduation begins at 20 c.c. and extends to 26. In the larger one it begins at 50 c.c. and extends to 56. Both are divided in .05 c.c.

*Experiment.*—The thoroughly dry apparatus is suspended in water of exactly 15° C. and chloroform of 15° C. is added as far as the lowest division (20 or 50 c.c.). 100 (or 250) c.c. of the spirits under investigation, diluted exactly to 30 per cent. alcohol volume, and 1 c.c. (or 2.5) sulphuric acid (sp. gr. 1.286) are added. The entire contents of the burette are run into the pear-shaped bulb. It is then shaken continuously and briskly about 150 times, after which it is again suspended in water at 15° C. After the chloroform has settled and the particles have been removed from the walls by tapping with the finger, the chloroform volume is read off on the scale. From this the "basis" is deducted. The "basis" is the increase in volume which the chloroform shows when shaken with pure ethyl alcohol free from fusel oil.

Since this is also dependent on the source of the chloroform employed, it must be determined anew when a different chloroform is used. The same sulphuric acid must also be used in all determinations.

The requisite pure alcohol is best prepared by fractional distillation, because even the commercial product known as "purest" is often unsatisfactory. The remaining operation is conducted as before. If now the "basis" be deducted from the increase of volume furnished by the spirits under investigation, the difference affords the increase due to fusel oil. From this the per cent. volume of fusel oil in the original spirits (not the 30 per cent.) may be found, when the smaller apparatus is used, by means of the following formula:

$$f = \frac{d(100+a)}{150}$$

where d represents the difference between the increase of volume found and the "basis," and a, the water or alcohol added which was necessary to dilute 100 c.c. original spirits to 30 per cent. volume. The formula depends on observations made by Stutzer and Reitmair, which show that every .15 c.c. increase in volume corresponds to .1 per cent. volume in the 30 per cent. alcohol.\*

In using this method the following points should be observed: The spirits under examination must equal exactly 30 per cent. by volume, *i. e.*, .96564 sp. gr. The most extreme limits allowable are 29.95-30.05 per cent. volume, because only  $\pm .1$  per cent. by volume alcohol causes an increase in volume of the chloroform of  $\pm .03$  c.c. corresponding to .02 per cent. by volume of fusel oil. The quantity of water which is necessary to dilute spirits greater than 30 per cent. by volume to 30 per cent. is found in a set of tables (also given in the "Chemiker Kalender").

The temperature must be kept as near 15° as possible while measuring the liquid and observing the volume. The utmost limits are 14.5-15.5°. As a correction for 15° for every .1° below normal temperature .01 c.c. is added. Above normal this amount

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\* In the larger apparatus .15 c.c. increase in volume represents .04 per cent. fusel oil.

is deducted. When fine spirits are investigated, in which minute quantities of fusel oil exert a great influence on the value, Stutzer and Reitmair recommend a concentration by fractional distillation when small quantities are present.

Since this concentration can only be extended to .15 per cent. by volume, it is necessary beforehand to ascertain if this limit is not already overstepped in the original product. Should this not be the case, 1000 c.c. spirits are added to 100 grs. dry potash, or if the spirits contain lower than 90 per cent. by volume of alcohol more potash is added. It is placed in a large distilling bulb and distilled from a salt-bath after 2-3 hours. The first 500 c.c. which distil over are collected separately, as are every subsequent 100 c.c. After all has distilled over, the flask is allowed to cool, 200-250 c.c. water are added and 100 c.c. are distilled off. This aqueous distillate is used to dilute the last fraction which contains the entire fusel oil, providing that the latter in the original spirits did not exceed .15 per cent. This fraction is placed in the agitator. The "basis" determination can be conducted with one of the intermediate fractions which is diluted to 30 per cent. by volume. When liquids are examined which contain substances having an influence on the volume increase (aldehydes, ether varieties, volatile acids and others increase; ethereal oils decrease the volume), such as brandy, liquors, etc., a distillation with potassium hydrate must be carried out in order to free from these. For this purpose 200 c.c. sample are placed in a spacious distilling bulb. Four-fifths of the volume is distilled off, the distillate is caught in a 200 c.c. flask and diluted to the mark with water of 15° temperature.

(β) Traube's method, using the stalagmometer. This depends on the observation that the size of the drops, that is the volume of the drop which issues from a capillary tube on a circular smooth surface, bears a definite relation to the quantity of fusel oil present. The apparatus consists of a bulb drawn out at both ends to a tube. One tube, the exit tube, is widened at the end to a disk which bears a capillary widened below to a cone-shaped opening. A constant volume is confined between two marks placed on the tubes. On the instrument is etched the number of drops which this volume yields when filled with a 20 per cent. pure spirit of a definite temperature. The correction for the above directions, at a

different temperature, is to be found in an explanation which accompanies the apparatus.

The spirits to be investigated are diluted to 20 per cent. volume. The requisite quantity of water is to be found in the tables referred to under Rose's method, after the density has been determined with a pyknometer. When ethereal oils are present in the spirits, it must be distilled first and the distillate then diluted. After the liquid has arrived at the temperature of the room, it is forced into the well-cleaned and dried apparatus by suction until the upper mark is reached. Care must be taken that no air bubbles enter. The liquid is then set at the upper mark and allowed to run out to the lower mark. Meanwhile the drops are counted. The last adhering drop is taken into account. According to Traube, the maximum error should not exceed .2 of a drop for every 100 c.c. By this operation .1 to .05 per cent. fusel oil can be determined. When smaller quantities, as low as .02 per cent., are present, he advises a concentration by agitation with ammonium sulphate solution, which dissolves fusel oil. By distillation of this the fusel oil is obtained in more concentrated form. The calculation is made from the difference between the number of drops counted and that designated on the instrument, corrected for prevailing temperature. The next lower difference on the accompanying tables is found and the fusel oil of the 20 per cent. spirit is gotten in per cent. by interpolation. If the amount of fusel oil in the tables = b and the water necessary to dilute 100 c.c. original substance to 20 per cent. volume = a, the fusel oil in per cent. by volume (f) in the original spirits would be

$$f = \frac{(100+a)}{100} b$$

#### **6. Methyl Alcohol (Wood Spirit).**

This finds use in the dyestuff industry, as well as for "denaturizing" spirits of wine.

Impurities usually present in wood spirit are: Aldehyde, acetone, methyl acetate, dimethylacetal, allyl alcohol and ethyl alcohol. The quantitative estimation of acetone alone will be described here.

The methods applied here are based on the fact that in the pres-

ence of alkali, acetone is changed to iodoform by iodine, whereas methyl alcohol and the other substances present do not bring about this formation. According to the method of Messinger, which is to be described, a definite quantity of iodine is added to form the iodoform, and the excess of iodine is titrated back. 1-1.5 c.c. wood spirit are placed in a 250 c.c. bottle. 20 c.c. normal alkali are added and followed by 20-30 c.c.  $\frac{1}{5}$  normal iodine solution. The whole is shaken briskly for  $\frac{1}{2}$  minute. The alkali is now exactly neutralized with hydrochloric acid (20 c.c. normal acid) and the excess of iodine is titrated back with a  $\frac{1}{10}$  normal hypo-sulphite solution, using starch paste as an indicator.

The number of grams acetone in 100 c.c. wood spirit ( $y$ ) is found by the equation :

$$y = \frac{m}{n} \cdot 7.612,$$

where  $m$  represents the quantity of iodine used in the formation of iodoform, and  $n$ , the quantity of wood spirit used in the analysis, expressed in c.c.

## VIII. Fats, Waxes and Mineral Oils.

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FATS are mixtures of triglycerides of monobasic fatty acids. Vegetable and animal waxes are fatty acid esters of higher fatty alcohol. Mineral waxes and mineral oils consist of hydrocarbons.

The groups named, representing different chemical constitutions, show characteristic behavior towards alkalies. Fats are saponified on treatment with alkali into salts of fatty acids (soaps) and glycerin, both of which are soluble in water. Fats are therefore completely saponifiable. Vegetable and animal waxes yield salts of fatty acids soluble in water, and insoluble higher fatty alcohols, by this treatment, and are termed incompletely saponifiable. Mineral waxes and oils are not changed by alkalies ; they are unsaponifiable.

### A. Fats.

#### 1. General Methods of Investigation.

Although the fats represent mixtures of many triglycerides, the quantity of the same in every kind of fat is a fairly constant one. In consequence of these so-called constants, slightly varying values can be determined for each fat. These would lead with certainty to the identification of the same. Of these constants there will be described :

(a) The saponification number. This indicates how many milligrams potassium hydrate are necessary to saponify one gram of fat, and is therefore a representation of the capacity of saturation of the fatty acid contained in the fat.

(b) Hübl's iodine number. This represents the quantity of iodine which a fat is capable of absorbing and serves as a measure for the unsaturated acids present (oleic acid, linoleic and linolenic acid series).

(c) The acetyl number, which is a measure for the oxy fatty acids and the fatty alcohols present.

(d) The acid number, which expresses the number of milligrams potassium hydrate used to neutralize the free fatty acids in a gram of fat. It serves, therefore, as a measure for the free fatty acids contained in the fat.

(a) *Saponification Number. (Köttstorfer's Number.)*

There are necessary to determine the saponification number :

(a) An about  $\frac{1}{2}$  normal hydrochloric acid, exactly standardized by titration with potassium hydrate.

(β) An alcoholic potash solution, prepared by dissolving in a little water 30 grs. caustic potash, purified by alcohol, and then diluting to 1 liter with alcohol free from fusel oil. After standing one day it is filtered into a flask. A 25 c.c. pipette, provided above with a piece of rubber tubing and a clip, is inserted into the single perforation of a tightly-fitting rubber stopper. When pure alcohol is used the solution will never become brown, but can at the utmost assume a pale yellow tint on standing for months.

To conduct the operation 1-2 grs. are placed in a wide-necked flask of 150-200 c.c. capacity. For the purpose of weighing, a small bottle with a lip is preferable. Introduce 50-60 drops oil from the weighing-bottle into the flask and reweigh the bottle. 25 c.c. alcoholic potash are now allowed to flow from the pipette into the flask. The drops which issue finally are counted, in order to observe equal conditions. A reflux condenser is then inserted through a suitable cork in the flask and the contents are heated to boiling in a water-bath and agitated from time to time. Saponification is complete in 15 minutes as a rule, but with difficultly saponifiable fats  $\frac{1}{2}$  hour is required. A few drops of phenolphthalein are added,\* and the excess of alkali is titrated with  $\frac{1}{2}$  normal hydrochloric acid.

Since the standard of the alcoholic potash alters somewhat, 25 c.c. are titrated anew with hydrochloric acid prior to each experiment. The same conditions as heretofore are to be observed, namely, the same period of heating on the water-bath, etc. The difference between the number of c.c. hydrochloric acid used for

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\* It is advisable to use alkali blue when the solutions are colored.

this and the previous titration is expressed in milligrams K O H and calculated on 1 gr. fat to obtain the saponification number.

(b) *v. Hübl's Iodine Number.*

Whereas iodine acts but slowly on fats, unsaturated fatty acids readily form chlor-iodine addition products on treatment with an alcoholic solution of iodine and mercuric chloride.

The materials necessary for this operation are :

(a) Iodine solution. 25 grs. iodine and 30 grs. mercuric chloride are each separately dissolved in 500 c.c. 95 per cent. alcohol free from fusel oil. The latter solution is filtered if necessary. They are then united.\* The liquid should stand 24 hours before using, because the standard rapidly alters at first. A 25 c.c. pipette may be inserted, as before.

(b) Sodium hyposulphite solution. It is made approximately  $\frac{1}{10}$  normal. The standard is best established with a potassium bichromate solution containing 3.874 grs. to the liter. 10 c.c. of this solution equal .1 gr. iodine.

(c) Chloroform. 10 c.c. of this, mixed with 10 c.c. Hübl's solution, should require, after 2-3 hours, the same amount of hyposulphite as this quantity of iodine solution used alone.

(d) Potassium iodide solution. 1 part potassium iodide to 10 parts water.

(e) Starch solution. Freshly prepared 1 per cent. starch paste. From .15-.18 gr. drying oils, .25-.35 gr. non-drying oils, or .8-1 gr. solid fats is placed in a 500 c.c. flask, provided with a tight-fitting stopper. 10 c.c. chloroform and 25 c.c. iodine solution are added. Should the liquid on shaking remain turbid, more chloroform is added. Should the liquid become colorless on brief standing, another measured portion of iodine solution is added, so that, in fact, on standing 6 hours the liquid still appears dark brown. Subsequently 20-25 c.c. potassium iodide and 200-300 c.c. water are added. Any red precipitate of mercuric iodide which forms is re-dissolved by addition of more potassium iodide. Sufficient hyposulphite is added, with frequent agitation, to render the aqueous liquid and the chloroform light in color. Starch paste is then

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\* Waller states that Hübl's iodine solution is much more stable when 25 c.c. hydrochloric acid (sp. gr. 1.19) are added to 500 c.c. of the same.

added, and the solution is carefully titrated to disappearance of the blue color. A similar experiment is simultaneously conducted with 25 c.c. iodine solution by titrating hyposulphite. From the difference the iodine absorbed is found and calculated into per cent.

Results are concordant when sufficient iodine is added. The excess should about equal half the iodine absorbed. Titration should be made after the solution has stood 6 hours. Longer standing does not in any way influence the accuracy of the result.

(c) *Acetyl Number.*

The acetyl number of Ulzer and Benedikt expresses the number of milligrams potassium hydrate which are necessary to saponify the acetyl groups in 1 gr. acetylated fatty acids.

To determine this the free fatty acids must first be isolated from the fats, for which purpose 30 grs. fat are placed in a flask with 60-70 c.c. alcohol and 10 grs. potassium hydrate, dissolved in a little water. This is boiled on a water-bath with a reflux condenser to complete saponification. The latter is finished when, after addition of some water and shaking, the liquid remains perfectly clear. The excess of alcohol is evaporated on a water-bath. The remaining soap is dissolved in warm water and is poured into a beaker of 1 L. capacity. The solution is boiled with dilute sulphuric acid until the fats are completely melted. A current of carbonic acid is meanwhile run through to prevent bumping. Thereupon the acid fluid is siphoned off and the fats are again boiled with water. The acid liquor is again siphoned, and the operation is repeated until the liquid siphoned off no longer reacts acid. The acids are filtered on a hot-water funnel through a dry filter, and are acetylated by boiling 2 hours with an equal volume acetic anhydride in a flask provided with a reflux. The contents of the flask are poured into a beaker of about 1 L. capacity, are mixed with 500-600 c.c. water, and boiled for  $\frac{1}{2}$  hour. As before, carbonic acid is conducted through a capillary extending nearly to the bottom. After a time the water is siphoned off and the boiling with water is repeated three times, whereby all acetic acid is removed. Finally, the acetylated acids are filtered in an air-bath at about 80° through a dry filter. In a portion of the acetylated acids the saponification number is taken as in (a). This gives the "acetyl saponification

number." In another portion the "acetyl acid number" is determined in the manner described below, in the method for acid number. The difference between the two gives the acetyl number. If a fat contain no oxy fatty acids, its acetyl number will equal zero.

(d) *Acid Number.*

About 10 grs. fat are slightly heated in a flask with about 50 c.c. pure acid-free 95 per cent. alcohol while the liquid is agitated. Upon cooling, phenol-phthalein is added, and the solution titrated with  $\frac{1}{2}$  normal alkali until the red color appears. The number of milligrams potassium hydrate used, calculated on 1 gr. fat, yields the acid number. When free fatty acids are used the acid number is identical with the saponification number. Frequently the acid number of a fat is expressed in Burstyn degrees. These express the number of c.c. normal alkali necessary to combine with the free acids present in 100 c.c. of the fat. The determination of acid number is also made use of in examining other fats, such as those used as lubricants.

The following tables\* contain the iodine numbers and saponification numbers of the most important fats :

Fats.	Iodine Number.			Saponification Number.		
	Min.	Max.	Mean.	Min.	Max.	Mean.
Olive oil.....	79	88	82-83	185	196	193
Sesamé oil .....	103	112	108-109	187	192	190
Peanut oil (Arachis oil).....	87.3	103	94-96	190	197	194
Cotton oil.....	102	112	108-109	191	198	195.5
Castor oil.....	82	85.9	84.5	176	183	180
Rape-seed oil.....	98	104	100-101	175	179	177
Linseed oil.....	170	183	178	187.4	195.2	192
Hemp-seed oil.....	140.5	157.5	150	190	193	191.5
Sunflower-seed oil.....	122	134	128	189	194	192
Cod-liver oil.....	123	166	144-148	175	194	182-187
Palm oil.....	51	52.4	51.5	200	202.5	201.5
Cocoanut oil .....	8	9.35	8.5	253	262	257
Butter fat .....	26	35	33	221	227	224
Tallow .....	35.5	44	39	193	206	197
Bone fat.....	46	55	49	...	...	190.9

\* The maximum and minimum values expressed in the tables are those found only in isolated cases. Normal values are those under the heading "Mean."

In addition to the determinations mentioned, the density is usually taken. This is done with the liquid fats in a pyknometer. Since, however, the densities of one and the same fat may vary considerably, and, moreover, since these are approximately the same for different fats, it is only seldom that they offer a reliable insight.

Certain features will be stated, in the chapters devoted to wax, mineral oils and soaps, concerning determination and estimation of unsaponifiable constituents of common resin and colophonium rosin.

## 2. Classification of Fats.

This is represented in the following scheme :

a. Liquid fats.

- a. Drying oils.
- β. Non-drying oils.
- γ. Fish oil.
- δ. Fluid waxes.

b. Solid Fats.

(a) *Liquid Fats.*

(α) Drying oils. These consist mainly of glycerides of linoleic acid and linolenic acid. In thin layers they dry to varnish-like masses in the air, thereby absorbing much oxygen, but they do not yield elaidin.

(β) Non-drying oils. They contain much olein, and dry with the utmost difficulty in the air or at higher temperatures. They absorb little oxygen and give elaidin.

(γ) Fish oils, obtained from the fats of fish, absorb much oxygen, do not dry to a varnish, and yield little or no elaidin. They give intense colorations with caustic soda, sulphuric acid, nitric acid and phosphoric acid, of which that obtained with sulphuric acid serves to distinguish them from other oils. It is obtained by warming 5 vols. oil with 1 vol. glacial phosphoric acid. By this treatment, all fish oils, whether mixed or not, give an intense red, brown-red or brown-black shade.

(δ) Liquid waxes from the oils of marine animals consist mainly of esters of monatomic alcohols, and contain only a small amount of glycerides.\* They are, like true waxes, only partially saponi-

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\* The classification of these under the fats is, therefore, a more or less arbitrary one.

fiable, and possess, in consequence, a very low saponification number. The unsaponified portion is solid and consists of monoatomic alcohols. They contain only 60–65 per cent. fatty acids, as against 95 per cent. in other oils. They absorb little oxygen in air, do not dry, and give no elaidin.

*Recognition of drying and non-drying oils.*—Since the thorough drying of the oils in air, spread on glass plates in thin layers, requires too long a period, the determination can hardly furnish a means of recognition. On the other hand, the following methods are suitable elaidin tests. This depends on the fact that glycerides of the oleic acid series are transformed by nitrous acid into the solid glycerides of the elaidic acid series, whereas those of the linoleic series, etc., remain liquid.

10 grs. oil, 5 grs. nitric acid, 40–42° Bé. and 1 gr. mercury are placed in a test-tube and are shaken continuously for 3 minutes to dissolve the mercury. The liquid is then allowed to stand for 20 minutes, and is then shaken for 1 minute. From this point olive oil will, for instance, solidify in 1 hour, peanut oil in 1 hour and 20 minutes, sesamé oil in 3 hours and 5 minutes, whereas linseed oil and fish oil give a red pasty foam and hemp-seed oil remains unaltered.

Copper may be used in place of mercury.

*Maumenee's test.*—This depends on the phenomenon that sulphuric acid, mixed with drying oils, heats up considerably more than with non-drying oils. The test is conducted as follows: 50 c.c. oil are placed in a 100 c.c. beaker. The temperature is taken with a thermometer, and from a pipette 10 c.c. conc. sulphuric acid of the same temperature are run in during a period of 1 minute, while the liquid is being stirred with the thermometer. To prevent loss of heat the beaker containing the oil may be placed in a second larger beaker, with cotton placed between. It is stirred until the temperature ceases to rise. Should the rise equal more than 70°, drying oils can be considered present with certainty. As examples,\* olive oil shows a rise of 41–43° in temperature, rape-seed oil 51–60°, and linseed oil 104–111°.

*Iodine number.*—The non-drying oils possess lower iodine

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\* According to Allen.

numbers than the drying oils. The iodine number, in consequence, serves as a convenient and safe means of identification, providing that fish oils are absent. These are non-drying, and yet possess a high iodine number.

(b) *Solid Fats.*

Recognition of solid fats is accomplished chiefly by :

(a) Specific gravity. This is best determined by the method of Gintl, who uses a small cylindrical, flat-bottomed pyknometer, the opening of which may be closed with a ground glass plate. When filling in the molten fat an excess is allowed to remain above the top. After cooling, the plate is slipped on and screwed down. The excess is wiped off with a cloth dipped in petroleum ether. The weights of empty and filled flasks are determined in the usual manner.

According to the method of Hager for the determination of specific gravity, the molten fat is allowed to drop a short distance into a glass dish filled with 60-90 per cent alcohol. The solidified drops are placed in the liquids which serve to determine specific gravity. For densities less than water a mixture of water and alcohol, and for greater densities a mixture of glycerin and water or alcohol, or alcohol and water respectively. Glycerin or glycerin and water are added until the drop just floats on the liquid, which is set in rotation. Finally the liquid is poured through glass wool, and the specific gravity, which is equal to that of the fat, is then determined with areometer or pyknometer. The determination of the specific gravity of molten fats may be conducted with the Westphal balance. The vessel containing the fat is placed in a paraffin bath.

(β) The melting point and solidification point of a fat and of isolated fatty acids. Fuller directions will be given in the discussion of tallow and wax.

(γ) The behavior in the refractometer. The latter is used chiefly in testing butter, fat and lard. For apparatus and description see Benedikt and Ulzer, Analyse der Fette und Wachsarten, 3. Aufl.

(δ) Saponification and iodine numbers. The saponification and iodine numbers of the most important fats are given in the tables, p. 113.

(7) Volatile fatty acids. These are determined by the Reichert-Meissl number, which represents the number of c.c.  $\frac{1}{10}$  normal alkali which are necessary to neutralize the volatile fatty acids in 5 grs. fat.

About 5 grs. fat are placed in a 200-300 c.c. flask on a water-bath with about 2 grs. stick potash and 50 c.c. of 70 per cent. alcohol and saponified.\* The flask and contents are shaken from time to time.

The alcohol is volatilized after complete saponification until a thick soap remains. This is dissolved by warming with 100 c.c. water. 40 c.c. sulphuric acid (1 : 10) and a few pieces of pumice-stone are added to the flask, which is then connected with a Liebig condenser by means of a bulb tube. It is first heated with a small flame until the fats have melted to a clear layer, after which it is distilled for a half hour and exactly 110 c.c. distillate are collected in a graduated flask. After shaking, 100 c.c. are filtered off in a measuring flask, emptied into a beaker and titrated with  $\frac{1}{10}$  normal alkali, using phenol-phthalein as indicator. The quantity of the alkali used is increased  $\frac{1}{10}$  and calculated on 5 grs. fat.

The Reichert-Meissl number is principally used to identify butter and cocoanut oils. Butter has a number between 26-29; cocoanut oil, 7.

### 3. Examination of a Few Common Fats.

#### (a) Olive Oil.

The iodine number and saponification numbers are taken. Should these correspond to the mean values given in the table, the oil may be considered pure. Should the saponification number correspond, but the iodine number lie above 85, adulteration with sesamé oil, peanut oil, or cotton-seed oil has been attempted. The methods, specially described, may be used for detecting their presence.

Should the saponification number be low and the iodine number high, the adulterant is presumably rape-seed oil. In this case a test for mineral oil must also be made. When used for machine oil the acid number should not exceed 16.

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\* Kreiss and some others recommend the use of sulphuric acid instead of potash.

*(b) Rape-seed Oil.*

The normal values for iodine and saponification numbers, as a rule, suffice for identification. Drying oils and fish oil raise the iodine and saponification numbers. Rosin oil and mineral oil lower the same. When used for lubricating purposes the acid number should not exceed 6.

*(c) Castor Oil.*

Iodine number and saponification number, acetyl number and density, serve to determine the purity. The acetyl number should not exceed 15.2; the density, .960-.966. Castor oil must completely dissolve in two parts by volume of 95 per cent. alcohol, and remain insoluble in petroleum ether.

*(d) Sesamé Oil.*

This is frequently adulterated with cotton-seed oil. Iodine number, saponification number and density do not afford sufficient means for identification. The Livache test is particularly suited to this purpose. It depends on the fact that the increase in weight due to oxygen absorption is perceptibly less in the presence of cotton-seed oil than in the genuine article.\*

The test of Livache is conducted by precipitating the solution of a lead salt with zinc. The precipitate is quickly washed with water, alcohol and ether, and dried in a vacuum over sulphuric. Two quantities of lead powder, each 1 gr., are spread out on two large watch crystals. The weight of each lead powder and crystal are taken and 20 drops of oil placed on one of the watch crystals from a finely-drawn-out pipette. On the other is placed the same quantity of the fatty acids of the same in such a manner that the drops do not flow together. Both watch crystals are again weighed in order to obtain the weight of oil and fatty acids and are set in a place protected from dust. They are allowed to remain in the light on the average seven days at ordinary temperature. When this time has elapsed, the increase in weight of each is determined and reckoned in percentage of substance taken. Presence of cotton-seed oil is detected by this means.

\* The increase in weight of the oils and fatty acids of oils, such as sesamé and most of the others, in the same time, is of nearly equal percentage.

*Detection of sesamé oil in other oils.*—According to Baudouin, 20 c.c. oil under investigation are placed in a test-tube containing 1 gr. cane sugar and 10 c.c. hydrochloric acid (sp. gr. 1.19). It is well shaken for a minute and allowed to settle. The layer of liquid, which separates immediately, as a rule, shows an intense red color in the presence of sesamé oil, whereas, in absence of same, the aqueous layer remains colorless at least 2 minutes and the oily layer appears green or yellow.

Villavecchia and Fabris attribute the red coloration to the furfural formed from the laevulose, which is formed by the action of hydrochloric acid on cane sugar, and demonstrate this by showing that a 2 per cent. alcoholic solution of furfural gives the same reaction. They therefore propose the use of this reagent in place of cane sugar.

(e) *Arachis Oil. (Peanut Oil.)*

This is characterized by the iodine number and saponification number given in the tables as well as the rise of temperature, which equals 45.5–51.4° with Maumené's test. Additions of peanut oil to other oils can be detected, according to De Negri and Fabris, by the fact that the soap solutions obtained in the saponification number solidify comparatively easy. An olive oil diluted with 10 per cent. peanut oil after determination of the saponification number gives a turbid liquid which subsequently deposits a precipitate of the potassium salt of arachidic acid.

The presence of arachidic acid, which melts as high as 75°, in peanut oil can be serviceable in detecting the latter when present in other oils. The procedure of Renard, modified by De Negri and Fabris, is conducted as follows:

10 grs. sample are saponified. The fatty acids are separated with hydrochloric acid, dissolved in 50 c.c. 90 per cent. alcohol, and precipitated in the cold with a solution of lead acetate. It is decanted after standing 12 hours. The residue is digested with ether to separate lead oleate, and the precipitate, consisting of lead palmitate and lead arachitrate, is separated from the liquid by decantation. It is finally filtered, and the precipitate is washed with ether until the filtrate no longer shows a residue on evaporation. The lead salts are decomposed in a separatory funnel with hydrochloric acid (1 : 5). Ether is added, the liquid is agitated, and when the

two layers have separated the aqueous portion is run off. The ethereal layer is then withdrawn, the ether is distilled off, and the residue, consisting of fatty acids, is dissolved in 50 c.c. hot, 90 per cent. alcohol. Upon cooling, a copious crystalline precipitate of arachidic acid separates. It is filtered and washed at first with 90 per cent. alcohol, and later with 70 per cent. alcohol, is weighed, and the melting point is taken. The latter usually is 70-71°, because the acid is not quite pure.

(f) *Tallow.*

In addition to the constants, the determination of the freezing point of the fatty acids, the so-called "titer test" is of especial importance. In order to obtain concordant results, the following method was proposed by Wolfbauer:

25 c.c. potassium hydrate, sp. gr. 1.509 (125 grs. stick potash in 100 c.c. water), are stirred with 120 grs. molten sample in a beaker. The temperature should be only slightly above the melting point of the tallow. It is placed in a compartment at 100° after being agitated, mixed, and covered with a watch glass. It is permitted to remain there, with occasional stirring, until the saponification is complete, and a drop, warmed with 50 per cent. alcohol, completely dissolves, which is the case after about 2 hours. 150 c.c. boiling water are stirred into the soap, which is then poured into a dish, treated with 165 c.c. sulphuric acid, sp. gr. 1.143 (22 c.c. conc. sulphuric acid and 150 c.c. water), and boiled until the fatty acids form a perfectly clear layer.

The acid liquid is withdrawn entirely with a siphon and the fatty acids are boiled with weak sulphuric acid (5 c.c. conc. sulphuric acid in 100 c.c. water), which is then again withdrawn, after which they are twice boiled out with 100 c.c. water. The fatty acids are eventually dried for 2 hours at 100°. The solidified acids are melted in a water-bath and filled to within 1½ cm. into a thin wall test-tube of 15 cm. length and 3.5 cm. diameter. The test-tube is then suspended in a specimen bottle by means of a cork. Thereupon a thermometer, graduated in one-fifth degree as far as 60°, is inserted through a cork into the fatty acids in such a manner that while four-fifths cm. distant from the bottom it is submerged to 35th division.

The clear mass is stirred with the thermometer until no longer transparent, and until the thermometer-reading on repeated stirring no longer changes. The thermometer is then fastened. The mercury begins to rise, due to liberation of latent heat of fusion. The highest mark which it touches, and at which it becomes stationary, is read off and taken as the freezing point. The difference between two determinations should not exceed  $.1^{\circ}$ . Frequently the iodine number of the fatty acids of tallow is taken. The number multiplied by  $1.1102$  gives the oleic acid in the fatty acids. When used for lubricating purposes, tallow should not contain more than .5 per cent matter insoluble in chloroform.

## B. Waxes.

As has been mentioned, waxes are of animal and vegetable origin. They are partly saponifiable and separate insoluble higher fatty alcohols. Mineral waxes are unsaponifiable. The saponification number affords a sure basis of distinction.

### 1. Vegetable and Animal Waxes.

Following determinations are chiefly resorted to in examining vegetable and animal fats: Acid number, saponification number, ester number (the difference between saponification and acid numbers), specific gravity, melting point and freezing point. These determinations are generally conducted according to the methods previously mentioned.

The specific gravity can be determined, in addition to the methods already given, with the Sprengel tube. This is a U tube (Fig. 10) of about 18 c.c. capacity and 11 mm. external diameter, which tapers at both ends to narrow bent tubes *a* and *b*, of which the one is longer and is provided with a mark, *m*. The molten fat or wax is brought into the tube by suction, during which operation the longer bent tube is dipped in the fat. It is now brought into a water-bath of constant temperature until the wax ceases to expand, and the excess in the shorter arm is removed with filter paper

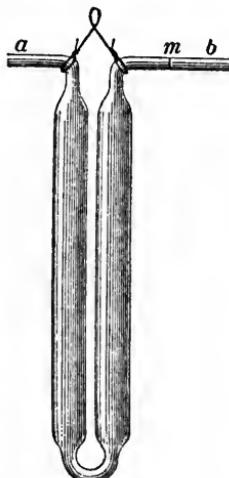


FIG. 10.—Sprengel Tube.

until the longer arm is just filled to the mark. It is allowed to cool, and the tube is cleaned and weighed. The experiment is repeated with water at the same temperature or at  $15^{\circ}$ . The melting point, according to Pohl, is usually determined by finding the temperature when the wax fuses. To this end the bulb of a thermometer is dipped for a moment in the fat or wax, which is heated slightly above its melting point so that a film will remain on removing. The thermometer is allowed to stand a while and is then inserted through a cork into a long, wide test-tube so that the bulb rests 1 cm. from the bottom. The test-tube is held with a test-tube holder 2-3 c.c. over a tin shield or an asbestos plate which is carefully heated with a burner. The point is noticed at which the wax becomes transparent when a drop of molten wax will appear at the lower end.

Frequently the molten fat is drawn into a thin walled, not too narrow, capillary tube, so that a column of 1-2 cm. is formed. The end is then sealed, and the tube is fastened on a thermometer so that the column of fat is on a level with the mercury bulb.

As soon as the substance has solidified—better after 24 hours—the thermometer is placed in a 3 cm. wide test-tube containing the heat conductor (glycerin). The temperature is taken the moment the fat flows to a clear liquid.

#### **Examination of Beeswax for Adulterants.**

(a) Determination of total acid number. In consequence of the difficulty experienced in the saponification of many waxes with alcoholic potash, especially when they contain paraffin or ceresin, too low results are often obtained. Benedikt and Mangold therefore determine the total acid number instead of the saponification number, that is, the number of milligrams caustic potash required to neutralize 1 gr. of the mixture of fatty acids and alcohol which is set free from the wax by saponification of the wax and subsequent decomposition of the soap obtained by boiling with dilute hydrochloric acid. The mixture is termed "decomposed wax." In order to prepare the latter 20 grs. potassium hydrate are dissolved in 15 c.c. water in a hemispherical capsule of 350-500 c.c. capacity. The solution is heated to boiling, when about 20 grs. previously-melted wax are stirred in. The solution is heated 10 min-

utes, with constant, brisk stirring, over a small flame. 200 c.c. water are added, the mass is heated and acidified with 40 c.c. hydrochloric acid, previously diluted with a little water. Thereupon it is boiled until the upper layer becomes perfectly clear. It is allowed to cool and is boiled out three times with portions of water, to the first of which hydrochloric acid has been added. The cake is finally removed, wiped off with filter paper, is melted in a drying oven and filtered. The filtered fat is poured, still liquid, on a watch crystal, and is broken up after cooling. For the estimation of total acid number 6-8 grs. of the decomposed wax so obtained are covered with alcohol free from acid, are heated on a water-bath, and titrated after addition of phenol-phthalein. Even when a large amount of ceresin is present, the saponification is usually complete. The total acid number lies somewhat lower than the saponification number, about 92.8 on an average, according to v. Hübl.

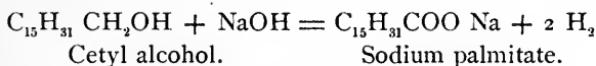
(b) Determination of ceresin and paraffin.

The quantity of paraffin or ceresin present may approximately be ascertained on the basis of the total acid number S by means of the following formula :

$$P = 100 - \frac{100 S}{92.8},$$

where P = paraffin or ceresin and 92.8 the average total acid number of pure beeswax.

The test of A. u. P. Buisine is useful in the exact determination of the paraffin or ceresin. This depends on the fact that the fatty alcohols, on heating with soda-lime, disengage hydrogen with formation of the sodium salts of corresponding fatty acids according to the equation :



A subsequent extraction with ether or petroleum ether removes, beside paraffin and ceresin, only the hydrocarbons of the wax.\*

To accomplish this, 2-10 grs. sample are melted in a small porcelain crucible, and to it is added an equal volume of powdered caustic potash. It is stirred, and on cooling a hard mass is obtained.

\* The quantity of hydrocarbons in beeswax varies between 12-14.5 per cent.

which is pulverized and uniformly mixed with 3 parts soda-lime (for 1 part wax).

The mixture is now heated in a small flask or a test-tube, at 250°, for 2 hours. The powdered residue, if necessary, together with the adhering broken glass, is powdered and extracted in a flask or extractor with ether or petroleum ether. The liquid is filtered, if required, the solvent is distilled off, and the last adhering traces are vaporized in a current of air. The residue is weighed. If p = the percentage of hydrocarbons found, C the ceresin or paraffin, then, according to Mangold, if the hydrocarbons in genuine wax be taken at 13.5 per cent.:

$$C = \frac{100}{86.5} \frac{p - 1350}{100}$$

(c) Determination of stearic acid. Stearic acid heated with alcohol dissolves, together with ceresin, but, unlike the latter, it does not separate so readily on cooling.

Therefore, if 1 gr. wax be boiled for several minutes with 10 c.c. 80 per cent. alcohol in a test-tube 18-20 mm. wide, and allowed to cool to 18-20°, then, upon adding water to the solution, filtered into a similar test-tube, the liquid becomes slightly turbid if it contain pure wax, whereas, when stearic acid is present, a flocculent precipitate is formed. Even with only 1 per cent. stearic acid a perceptible precipitate is formed. On the strength of the acid number, the stearic acid may be approximately calculated. The acid numbers of pure beeswax and stearic acid are respectively 20 and 195. Let that of the sample = S. Then the stearic acid

$$K = \frac{100}{175} \frac{(S - 20)}{100}$$

The absence of other acids, including those of rosin, is taken for granted.

(d) Determination of neutral fat.

Since pure wax yields no glycerin, but fats contain an average of 10 per cent., the neutral fat may be approximately determined on the strength of the amount of glycerin present, by multiplying the latter, which is found by the permanganate method (see Glycerin, p. 141) by 10.

(e) Determination of carnauba wax.

When present, this wax decreases the acid number, while the ether number remains unchanged. Specific gravity and melting point are increased.

(f) Determination of rosin. The most applicable qualitative test for rosin is the reaction of Morawski and Storch (see Mineral Oils, p. 129). The methods of Twitchell or Gladding (see Soaps, p. 137) may be used for quantitative purposes, but in this case myricyl alcohol and other unsaponified matter must previously be removed from the saponified sample.

## 2. Mineral Waxes.

Melting point, freezing point and specific gravity are the tests applied to mineral wax. The methods employed by buyer and seller should be identical, because the results obtained by different methods differ not inconsiderably. The insolubility of ceresin and paraffin in boiling acetic anhydride distinguishes these from the fatty alcohols. The latter remain entirely dissolved in the heat and partially in the cold.

The loss of weight of ozokerite (earth wax) on heating at  $150^{\circ}$  is also determined. It should not exceed 5 per cent. The earthy constituents are determined by dissolving in benzine and weighing the residue.

The following table contains the most important data of the most common waxes:

Wax.	Specific Gravity at $15^{\circ}$ .	Melting Point.	Freezing Point.	Acid Number.	Saponification.	Iodine Number.
Carnauba wax.....	0.990—0.999	$83^{\circ}$ — $85^{\circ}$	$80^{\circ}$ — $81^{\circ}$	4—8	80—95	13.5
Beeswax.....	0.958—0.975	$62^{\circ}$ — $65^{\circ}$	$60.5^{\circ}$ — $62^{\circ}$	18.6—21	91—97	8—11
Chinese wax.....	0.926—0.970	$81^{\circ}$ — $83^{\circ}$	$80.5^{\circ}$ — $81^{\circ}$	.....	63—77.9	.....
Spermaceti .....	0.942—0.960	$44^{\circ}$ — $47^{\circ}$	$43.4^{\circ}$ — $44.2^{\circ}$	0—5.17	125.8—134.6	.....
Paraffin .....	vary considerably.			.....	.....	.....
Ceresin .....	0.918—0.922	$61^{\circ}$ — $78^{\circ}$	.....	.....	.....	.....

## C. Mineral Oils.

Mineral oils are either distillation products of bituminous coal or bituminous shales, etc., or else their origin is crude petroleum, from which they are likewise gotten by distillation. Their use is mainly for lubricating and illuminating purposes. The higher dis-

tillation products of petroleum or shale, termed "heavy oils," are used as lubricants, while the lower boiling fractions of shale oil are used for illuminating purposes under the names solar oil, illuminating oil, and those from crude petroleum as petroleum.

The gas oils, likewise from shale oil, are used mainly in oil gas factories, while the lowest distillation products (light shale oil, photogen on the one hand; gasoline, naphtha, benzine on the other) are used as solvents for fats, etc.

### 1. Mineral Lubricants.

The viscosity, specific gravity, flash point, burning point, acidity, rosin, fatty oils, rosin oils, and, if necessary, coal-tar oils, are the tests usually undertaken.

(a) Viscosity. The viscosity or body of an oil is measured by comparing the time it takes for a given quantity of oil to flow from a narrow opening, with the time it takes an equal amount of water to flow out. The latter is taken as 1.

The most convenient of the viscosimeters is that of C. Engler (Fig. 11). The vessel containing the oil under investigation consists of a smooth box (*A*) of brass, provided with a lid (*A'*). The form and dimensions are indicated in the figure. Connected with the conical bottom is a 20 mm. long tube (*a*) which is almost exactly 3 mm. in width. It is usually made of brass. It may be opened and closed by means of a plug (*b*).

Four level-marks (*c*) serve to measure off the oil sample and to give means for keeping the level in the box horizontal. Filled to the mark, the apparatus should hold 240 c.c. The box (*A*) is surrounded by a jacket (*BB*) made of brass, and is open at the top. This serves to hold suitable fluid, by which the contents of *A* can be brought to the desired temperature.

The thermometers *t* and *t'* record the temperature of the oil to be tested and the liquid in the jacket. The apparatus rests on a tripod. The measuring flask *C*, under the exit-tube, is provided in its neck with the marks 200 and 240. The neck is enlarged, in order to shorten the escaping column.

*Regulation of the apparatus.*—240 c.c. water are placed in the box, which is previously cleaned with ether, alcohol and water, and plugged. The temperature is brought to 20°. To do this the

water contained in the jacket (*BB*) is maintained at this temperature until the inner thermometer registers exactly  $20^{\circ}$ . In the meanwhile the flask is allowed to drain. It is then placed under the vent and the plug is withdrawn. The time is recorded in seconds, by a second-watch or chronometer, which elapses while the flask is filled to  $200$ . Before allowing the oil to run out, it must have come to complete repose. The time required to issue should lie between

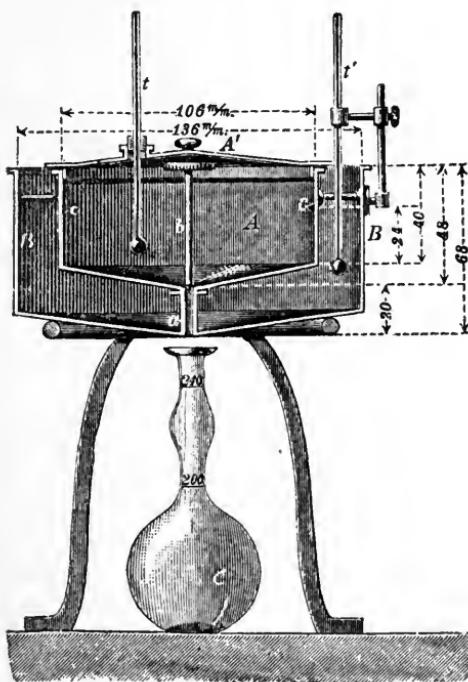


FIG. IX.—Viscosimeter of Engler.

50 and 55 seconds when the apparatus is properly constructed. The mean is taken of three determinations, which should not differ by more than  $\frac{1}{2}$  minute. This time is taken as 1.

*Oil test.*—In the next operation all moisture is removed from the box by drying and rinsing with alcohol, then with ether. The apparatus is filled to the mark with the oil in question. Only thin oils can be filled in with a measuring flask. It is then brought to

the desired temperature by heating the jacket (*BB*), which contains water or oil. The temperature must remain constant at least 3 minutes before the operation is begun. Determination of the time of issue is then conducted as before.

The lowest grade for an oil which is to be used as a lubricant is, according to Engler, a degree of viscosity of 2.6 at  $20^{\circ}$ , water = 1. With viscosity determination of lubricants the rule holds good that the temperature used should lie near that which the oil will assume while in use (machine oil  $50^{\circ}$ , cylinder oil  $150^{\circ}$ ).

In order to maintain an even temperature above  $50^{\circ}$  for a longer period, the later forms of apparatus are provided with a ring burner the gas flames of which heat the liquid in the jacket. In addition, the rod of the plug issues from an opening in the lid, so that it can be withdrawn without removing the lid. The liquid for the jacket and the oil, in this case as well as with the older forms of apparatus, should be heated to the required point and poured in.

Fatty oils as well as lubricants are subjected to the viscosimetric test. In many cases, such as rape-seed oil, the viscosity is so large and so constant that it can serve as a test for purity.

(*b*) Specific gravity is determined with an areometer or a pyknometer.

(*c*) Flash and burning points. A crucible 6 cm. upper diameter and 6 cm. high is filled with oil to within 1 cm. of the rim.

The mercury bulb of a thermometer is then immersed with the end 1 cm. above the bottom, which is best accomplished by first resting the thermometer on the bottom and subsequently raising the same 1 cm. The crucible is warmed in a sand-bath, and when the temperature has overstepped  $120^{\circ}$  a small flame, preferably a peased flame of a burner, is passed over the surface of the oil at the same height as the crucible rim at every increase of  $5^{\circ}$ . As soon as the first faint explosion of oil-vapor saturated air ensues the flash-point has been reached. The flame is enlarged, and when the temperature has increased  $10^{\circ}-15^{\circ}$  it is passed over the surface at every  $2^{\circ}$  increase until quiet ignition takes place. The burning point is so obtained. Draughts are prevented by screens of pasteboard.

The burning point of spindle oils should not lie under  $150^{\circ}$ ; that of machine oils (transmission oils) not below  $170^{\circ}$ .

(d) Acidity. Mineral oils should be entirely free from acids. The acid remaining after the refining process is detected by shaking about 100 c.c. oil with an approximately equal volume of tepid water to which several drops of methyl orange have been added. The aqueous layer, after settling, will appear red.

(e) Resins. Incompletely refined oils resinify readily. A test for resinous matter can be conducted by placing 20 c.c. sample, together with 10 c.c. sulphuric acid and 20 c.c. petroleum benzine, in a cylinder divided into 50 c.c., agitating and allowing to settle. The increase in volume of the sulphuric acid is read off. With good oils the increase usually amounts to 1.2-2.4 c.c., that is 6-12 per cent. of the oil volume. Under no conditions must it exceed 2.4 c.c. (12 per cent.).

(f) Fatty oils. Fatty oils are easily detected by the noticeable saponification number which they possess. A quantitative determination is conducted by the method which will be described later (p. 132).

(g) Rosin oil. For qualitative purposes the test of Storch-Morauski is to be recommended: 1-2 c.c. oil are shaken with 1 c.c. acetic anhydride. The liquid is allowed to settle, the acetic anhydride is pipetted off and treated with a drop of sulphuric acid (sp. gr. 1.53). In the presence of rosin oil a violet color is produced. The freezing point of an oil, which in use is subjected to winter temperature, is usually taken. Furthermore, the lubricating value is frequently determined by means of special complicated apparatus.

## 2. Petroleum (Illuminating Oil).

The valuation of petroleum as an illuminant is estimated by use of specific gravity, flash point, viscosity and distillation tests.

(a) Specific gravity. The areometer, less frequently the pyknometer, is used. Finer American oils have an average specific gravity .800; Galician oil .805-.820; and finer qualities Russian kerosene .815-.820. In general, too low a specific gravity indicates admixture with low-boiling oils, and, in consequence, danger from fire. A high specific gravity indicates imperfect separation from high-boiling oils. To use specific gravity alone as a criterion is altogether too unreliable.

(b) Flash point. Since 1882 the apparatus of Abel has been

used in the official testing of petroleum. It consists mainly of a petroleum receiver provided with a lid and warmed externally with a water-bath. The petroleum is filled in up to a designated mark. A thermometer inserted into the lid is immersed in the petroleum. In addition it is provided with openings which can be opened or closed by a slide worked simultaneously by means of a small piece of mechanism, with a small lamp suspended on trunnions. As the slide is made to recede, the small flame comes directly over the middle opening, and is there in direct contact with the petroleum vapors. As the slide is made to close the opening, the flame recedes. The water in the water-bath is heated to 54.5–55°. Continuous manipulation is started as soon as the petroleum approaches the expected flash point, and is repeated for every half degree rise in temperature until a sudden flash of blue light announces ignition. Exact description and instructions accompany the apparatus, on account of which a closer description is not necessary here. The minimum flash point allowed in Germany is 21° C.

(c) Viscosity. According to Engler, the viscosity of illuminating oil bears a direct relation to the speed of absorption in the wick. To conveniently determine this speed in an oil, therefore, the viscosity is taken. The Engler apparatus, possessing, however, a 1.8 mm. exit (instead of 3 mm.), is used.

(d) Distillation test (distillation curve). This is conducted in a distilling bulb of the following dimensions: Diameter of lower part 6.5 cm., diameter of neck 1.6 cm., length of neck 15 cm. The side tube should be 10 cm. long, .6 cm. wide, and attached at an angle of 75°. The distance from the place of attachment to the level of the 100 c.c. oil, with which the flask is filled, should be 9 cm. The side tube is attached to a condenser of 1 cm. average width and 45 cm. length. 100 c.c. petroleum are placed in the bulb with a pipette and are heated to boiling. A wire gauze is set under at first, but it is removed when the temperature has ascended above 150°. Distillation is conducted so that 2–2½ c.c. distil every minute. The fractions between every 25° or 50° are weighed or measured. As soon as a temperature of 150° is reached the temperature is allowed to sink at least 20° by removing the lamp. The contents are again brought to boiling, and are distilled

until the above temperature is again reached. This is repeated until nothing more distils up to that point. Results agreeing within 1 per cent. are thus obtained. The main fraction, 150–300°, is termed normal illuminating oil. The amount of same in especially well refined illuminating oils can reach 80 and even 90 volume per cent. A good illuminating oil should contain (according to Beilstein) not more than about 5 per cent. fraction under 150° and not more than about 15 per cent. fraction above 270°.

The test for acids can be conducted according to the method described under lubricating oil. The behavior toward conc. sulphuric acid is at times used as a test for purity of petroleum. On mixing with an equal volume of conc. sulphuric acid, and allowing to separate, the petroleum layer should be rather lighter and the sulphuric acid at the most only yellow, but never brown. The rise of temperature on mixing should not exceed 5°. A rise of temperature of 20–50° ensues when distillates from bituminous shales, rosin, etc., are present.

### 3. Gas Oil.

An approximate means of determining the gas contained in gas oil can be found in a gasification on a small scale by gasifying a definite quantity of the oil in a red-hot retort into which it is dropped, and measuring the gases formed. The Italian customs authorities prescribe the use of the method of Nasini and Villavecchia in testing gas oils. 100 grs. oil are distilled under reduced pressure (40 mm.) to a temperature of 210° and the distillate so obtained is distilled under normal pressure to 310°. The fraction should not exceed 20 per cent. of the total oil used.

## D. Products of the Fat Industry.

### 1. Materials Used in Oiling Wool.

Fatty oils, oleic acid, especially emulsion of oil and oleic acid, with small quantities of ammonia or soda and water, are used for this purpose. The fatty oils are also replaced in part by mineral oils, due to the fact that 80 parts mineral oil with 10 parts oleic acid and 10 parts  $\frac{1}{2}$  per cent. solution of soda emulsify very well. Mineral oil, when present, is frequently the cause of spots in the cloth. The oils from the scouring water are also used under the names elain, extract oil. The examination of other products em-

brates the determination of unsaponifiable matter, neutral fat, free fatty acids, alkali salts of fatty acids, and occasionally water and alcohol.

(*a*) Unsaponifiable matter. Qualitative test. A piece of stick potash, pea-size, is dissolved in 5 c.c. 95 per cent. alcohol. Three drops substance to be tested are added and the whole is boiled for a minute. Should turbidity ensue on addition of 3 c.c. water, unsaponifiable matter is present.

Quantitative determination. About 10 grs. substance are dissolved in 50 c.c. 95 per cent. alcohol, and to this are added 3 grs. caustic potash, dissolved in a very little water. By heating with a reflux on a water-bath for an hour, fatty acids and neutral fats are saponified. It is then diluted with 30 c.c. water and extracted in a separatory funnel with petroleum ether. Addition of alcohol assists the separation of the two layers. The soap solution so obtained is run off and extracted a few more times with petroleum ether. The collected petroleum extractions are shaken 1-2 times with a little water in order to free from dissolved soap. The petroleum ether is then filtered through a dry filter into a weighed flask. The solvent is then distilled off as much as possible, and the last adhering traces are removed by immersing the flask in a hot water-bath and conducting into it a current of air from a blast bellows. After about 15 minutes the flask is removed from the water-bath, is allowed to cool, and weighed. Air is repeatedly run through for 10 minutes at a time until the weight of the flask is nearly constant. The increase in weight represents the unsaponifiable matter of mineral oil nature.

(*b*) Total fatty acids. The soap solution contained in (*a*) is decomposed with dilute hydrochloric acid and shaken out with ether in a separatory funnel. The ether layer is separated, distilled, and the fatty acids in the residue are determined as in (*a*).

(*c*) Free fatty acids. About 10 grs. sample are dissolved in 50 c.c. alcohol (if necessary by heating) and titrated with normal alkali, using phenol-phthalein as indicator. The amount of alkali solution used is first of all recorded.

(*d*) Alkalies. The alkalies present in form of fatty acid salts are determined by heating 5-10 grs. sample with water, adding an excess of standardized sulphuric acid (about  $\frac{1}{2}$  normal), separat-

ing from the precipitated fat (fatty acids, neutral fat, unsaponifiable matter) by filtration or extraction with petroleum ether, and titrating back the excess of acid in the aqueous layer.

The nature of the alkali can be qualitatively proved in another portion. Attention is also called to the not infrequent presence of ammonium soaps.

(c) Mean molecular weight of the fatty acids. The determination is necessary to determine the exact quantities of free fatty acids, soaps and neutral fats. For this purpose the total fatty acids obtained as in (b) are dissolved in alcohol and titrated with normal alkali, using phenol-phthalein as indicator. Let  $g$  = the weight of fatty acids,  $u$  the number of c.c. normal alkali used, then  $M$ , the mean molecular weight, is gotten by the formula :

$$M = \frac{1000 \text{ g.}}{u}$$

Water and alcohol are sometimes present in wool oiling material. They are determined together by placing about 30 grs. ignited quartz sand in a platinum capsule and finding the weight of capsule + sand + small glass rod. About 5 grs. sample are weighed out in the dish and admixed by stirring. It is dried at 100° and the loss of weight is noted.

Calculation of the quantities of free fatty acid, soap and neutral fat present :

(a) The amount of normal alkali used in (c) is multiplied by the quotient of 1000 into the mean molecular weight. The free fatty acids are thus obtained.

(β) The quantity of alkali found, according to (d), is reckoned into fatty acids present in the form of soap, by means of the mean molecular weight.

(γ) If the free acids, as found in (a), as well as the fatty acids found present as soap, as in (β), be subtracted from the total fatty acids, there remains that which is present as neutral fat and which can be reckoned into neutral fat with sufficient accuracy by multiplying by  $\frac{100}{95}$ .

## 2. Soaps.

Soaps are mainly alkali salts of fatty acids, in fact, sodium and potassium salts.

Soda soaps are hard and come into the market under the name of compact soaps, cut or filled soaps. Potash soaps are soft and are known as soft soaps. Lately, however, hard potash soaps (Schicht's patent) have appeared. For many industrial purposes, substances such as rosin (rosin soaps), borax, water-glass, sodium aluminate, soda (to increase alkalinity), are added to soaps. Furthermore, adulterants, such as chalk, heavy spar, starch, clay, etc., etc., are frequently encountered.

#### Analysis of Pure Soaps.

These may contain, beside the alkali salts of fatty acids, free alkali, alkaline carbonates, free fatty acids and neutral fats.\* In addition, a considerable quantity of water is always present.

(a) Water. About 5 grs. of soap, removed from the center, in form of shavings, are dried at  $50^{\circ}$  for 1-2 hours. The temperature is then gradually raised to  $100-110^{\circ}$  and the soap is dried to constant weight.

Soft soaps are placed in a 100 c.c. beaker containing a small glass rod, and the bottom of which is covered 1.3 cm. deep with ignited quartz sand. Beaker + sand + rod are weighed.† About 5 grs. soap are added and the whole is reweighed. 25 c.c. alcohol are added, and the mass is heated on a water-bath and stirred. The beaker is then placed in a drying oven and dried to constant weight at  $110^{\circ}$ .

#### (b) Total fat and total alkali.

10-20 grs. fine cut soap are dissolved in about 100 c.c. hot water in a beaker. An excess of standardized sulphuric acid is added (50-80 c.c. normal acid) and the whole is heated in a water-bath containing boiling water until a clear layer of fatty acids is formed. It is now allowed to cool. In case the fatty acids refuse to solidify a weighed quantity of wax, paraffin or stearic acid, approximately equal in weight to the soap taken, is added, and the mass is re-heated and again allowed to cool. The fatty acid cake, now solid, is removed from the beaker with a glass rod, and is washed off with water. The washings are caught in the beaker. It is externally

\* Manifestly, a simultaneous presence of free alkali and free fatty acid is impossible.

† All weighings should be made as nearly as possible at the same time, because the quantity of water in soaps readily changes.

dried with filter paper and kept in a cool place. The solution remaining in the beaker is filtered, the filter is washed well, and the filtrate is titrated back, using methyl orange as an indicator. The total alkali, representing that combined with fatty acids, free alkali and alkaline carbonates, is calculated from the acid required for decomposition.

The total fat is determined by dissolving the particles adhering to the beaker in ether, filtering the latter through the previously employed filter into a weighed glass vessel containing a glass rod. After the ether has been volatilized, the fatty acid cake is also placed in the vessel and is heated with a small flame, with constant stirring, until the crackling sound, caused by escaping steam, has ceased, and the vapors of fatty acids have begun to make their appearance. Upon cooling, the glass dish is weighed and the added paraffin, etc., is deducted. The total fat is thus obtained. Any neutral fats, as well as fatty acids, will be present.

(c) Alkaline carbonates and free alkali.

*Qualitative test.*—A portion of soap is warmed and dissolved in alcohol, filtered, and any residue is washed with alcohol. Free alkali is detected by the red color which will form on addition of phenol-phthalein to the filtrate. On the other hand, the residue on the filter is dissolved in water and tested for alkaline carbonates by warming with phenol-phthalein.

*Quantitative determination.*—About 10 grs. soap are treated as above, care being taken, however, in washing with the alcohol, which is best done by using a hot water funnel during filtration.

The alcoholic filtrate, as well as the aqueous solution of the well-washed residue, is titrated with  $\frac{1}{10}$  normal acid, using phenol-phthalein as indicator in the first instance and methyl orange in the second.

After the free alkali and alkali carbonate have been deducted from the total alkali found, as in (b) (everything calculated as alkali oxide), there remains the alkali which is bound to the fatty acids. This can also be directly determined by dissolving a weighed quantity of soap in water, decomposing it with an excess of hydrochloric acid, thus using the separated fat in a moistened filter, washing, dissolving the fatty acid in alcohol by placing filter and contents in a beaker with alcohol, and finally titrating with alkali, using phenol-phthalein as indicator.

As a rule the alkali in hard soaps is calculated as sodium oxide and that of soft soaps as potassium oxide. On the assumption that both potash and soda are present in a soap, 5 grs. of the latter are burned in a platinum dish until only a charred mass remains. This is covered with water, filtered and washed. In the aqueous filtrate a check determination of total alkali may be conducted by titration with hydrochloric acid, after which a determination of potassium is made in the usual way with platinic chloride. (See *Fertilizers*, p. 73.)

(d) Free fatty acids. When the alcoholic soap solution does not change color on addition of phenol-phthalein (a proof of the absence of free alkali), free acid, which may be present, can be determined by titration with caustic soda.

(e) Neutral fat. A considerable quantity of fine shaved soap is weighed off, dried and extracted in a Soxhlet extractor with ether. In order to remove traces of soap which may perchance have gone into solution, the ethereal extract is shaken out 2-3 times with water in a separatory funnel. Then, if necessary, it is filtered, the ether is volatilized, and the residue is weighed after the usual treatment in a current of air. It also contains any free fatty acids which may have been present. The latter may be deducted after determination (d) has been made, or they may be directly titrated.

*Summary of analysis.*—The percentage of fatty acids must not be placed as such in the analysis, but must first be reckoned into anhydrides. No great error is experienced in simply deducting 3.25 per cent. from every 100 parts fatty acid.\*

In order to ascertain the nature of the fat from which a soap has been made the separated fatty acids are tested for melting point, freezing point, specific gravity, iodine number, saponification number, etc.

#### Determination of Foreign Admixtures in Soaps.

(a) Examination of residue insoluble in alcohol.

To determine the total amount of the same, a weighed quantity of soap is dried and warmed on a water-bath with 8-10 times the quantity of alcohol. It is then filtered through a weighed

\* Instead of this a quantity of water, equivalent to the alkali which is bound to fatty acids, may be deducted.

filter, washed with alcohol, dried and weighed. The residue is extracted with cold water and the solution is tested for chlorides, sulphates, carbonates, silicates and borates of the alkalies. If necessary, quantitative determinations of these constituents may be made in the usual manner.

The residue from the aqueous extraction is ignited to destroy organic matter, is weighed, and the ash is qualitatively and quantitatively examined. It is advisedly examined for chalk, clay, infusorial earth, etc.

Any organic matter, such as dextrine, contained perhaps in the residue from the alcohol extraction, is dissolved in cold water and can be reprecipitated from its aqueous solution by alcohol. Starch can be detected under the microscope as well as by the blue coloration with iodine.

(b) Glycerin, quantitative estimation. 1-10 grs. soap are dissolved in water or in methyl alcohol when organic substances, insoluble in methyl alcohol, are present. The solution is filtered, the alcohol is volatilized, the fatty acids are separated with dilute hydrochloric acid, and the glycerin in the acid filtrate is estimated according to the method of Benedikt and Zsigmondy. (See Glycerin, p. 141.)

(c) Rosin. In the qualitative test for rosin in soaps, or in the fatty acids separated from the latter, the reaction of Storch and Morowski (p. 129) is used. The method used in the quantitative estimation of rosin in the mixture of the latter with fatty acids, which is separated by mineral acids, has, until recently, been that of Gladding. It depends on the fact that the silver salts of fatty acids are insoluble in ether, whereas silver resinate is soluble in the latter. Lately preference has been given the method of Twitchell. It depends on the property of fatty acids forming esters when hydrochloric acid gas is conducted into their solution, whereas rosin does not react under the same conditions.

2-3 grams rosin-fatty acid mixture are dissolved in 10 times the volume of absolute alcohol in a flask. A brisk current of hydrochloric acid gas is led in. Meanwhile, the temperature is kept under  $20^{\circ}$  by good cooling. At first the gas is rapidly absorbed. After a period of about  $\frac{3}{4}$  of an hour the esters formed separate on the surface and further absorption ceases. The flask is withdrawn from

the cooling mixture, is allowed to stand  $\frac{1}{2}$  hour, is diluted with 5 times the volume of water, and boiled until the acid solution clarifies. The resinic acids can be determined either gravimetrically or volumetrically.

(a) Gravimetric method. The contents of the flask are placed in a separatory funnel and shaken up with petroleum ether. The acid layer is drawn off, the petroleum ether layer is washed and shaken up with a solution of 5 grs. caustic potash, dissolved in 5 c.c. alcohol and 50 c.c. water. The resin is saponified and the soap formed remains dissolved in the aqueous layer which separates completely from the petroleum ether layer. The soap solution is drawn off and the petroleum ether is washed first with dilute potassium hydrate solution and then with water.

The collected aqueous extractions are decomposed with dilute hydrochloric acid. The precipitated resinic acids are dissolved in ether, the ether is distilled off, and the residue is dried at  $100^{\circ}$  and weighed.

(β) Volumetric method. The contents of the flask are shaken up with about 75 c.c. ether in a separatory funnel, the acid layer is drawn off, and the etherial layer is washed with water until acid reaction with litmus paper has ceased. 50 c.c. alcohol are added and the solution is titrated with  $\frac{1}{2}$  normal alkali, using phenolphthalein as indicator. The resinic acids are saponified, whereas the fatty esters remain unattacked. The resinic acid equivalent is taken as 346 in the calculation.

### 3. Turkey-Red Oil.

Turkey-red oil is a product of reaction between concentrated sulphuric acid and chilled castor oil,\* to which ammonia has been added in quantity sufficient to impart the property of forming a complete emulsion when a sample is shaken with water. Turkey-red oil contains a water-soluble constituent consisting of "ricinol-sulphuric acid," and which can be salted out of its aqueous solution with salt, very dilute sulphuric acid and hydrochloric acid. The "ricinoleic sulphonic" acid is not decomposed by boiling water or alkali solutions, whereas, when boiled with dilute acids, it

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\* Sometimes other oils.

is converted into ricinoleic acid and sulphuric acid. That portion of turkey-red oil which is insoluble in water consists mainly of ricinoleic acid, and contains, in addition, some neutral fat, and perhaps polyricinoleic acids, together with anhydrides of ricinoleic acid and the above mentioned acids. Good castor oil should yield a fairly permanent emulsion with water, should dissolve to a clear solution in ammonia, and should not become turbid thereafter on addition of much water.

#### Chemical Examination.

According to Benedikt, this applies principally to the determination of total fat. In more exact analyses, the neutral fat, sulphonic acid, ammonia, soda and sulphuric acid are determined by the methods employed by the above author.

(a) Total fat. By this is understood the sum of the water-insoluble constituents of the acidified oil (fatty acids, oxy fatty acids and neutral fat) and the oxy fatty acids obtained by the decomposition of the soluble fatty sulphonic acids. About 4 grs. sample are stirred with 20 c.c. water, which are gradually added, in a thin hemispherical glass dish of about 125 c.c. capacity, which has previously been weighed, together with a small glass rod. When the liquid is turbid, a drop of phenol-phthalein is added, followed by ammonia to faint alkaline reaction. It is now mixed with 15 c.c. of sulphuric acid, is diluted with an equal volume of water and 6-8 grs. stearic acid are added, whereupon it is heated to faint ebullition. When the fatty acids have separated in a clear layer, it is allowed to cool. The solid cake is raised with a glass rod, rinsed with water, and placed on filter paper. The fat particles attached to the walls are collected by heating the liquid in the dish until the particles have united to 1 or 2 drops. The dish is removed from the water-bath and inclined, so that the drops reach the glass walls, where they immediately solidify and cling. The liquid is now poured off, the fat cake is placed in the rinsed dish and heated with a small flame in a manner similar to that employed in the total fat estimation in soap (p. 134). The cooled-off cake residue is weighed and the weight of stearic acid added is deducted.

(b) Neutral fat. About 30 grs. sample are dissolved in 50 c.c. water, 20 c.c. ammonia and 30 c.c. glycerin are added, and the mass is shaken out twice with quantities of 100 c.c. ether. Small

traces of soap, which are taken up by the ether, are removed by shaking with water. The ether is then distilled off and the residue is dried first in a water-bath, then in an air-bath, and is finally weighed.

(c) Soluble fatty acids. (Fatty sulphonic acids.) 5-10 grs. sample are dissolved in 25 c.c. water in a pressure flask. 25 c.c. fuming hydrochloric acid are added, and the flask is heated in an oil-bath at 130-150° for an hour. Its contents are then diluted with water, poured into a beaker and filtered from the fat layer. To insure easy manipulation an indefinite quantity of stearic acid may be added, the solution heated, and again allowed to cool. A sulphuric acid determination is made in the filtrate by means of barium chloride. The sulphuric acid found in (e) is deducted from this, and the remainder is calculated into ricinol-sulphuric acid. (80 parts sulphuric acid correspond to 378 parts ricinol-sulphuric acid.)

(d) Ammonia and soda. 15-20 grs. oil are dissolved in ether and shaken out 4 times with quantities of 5 c.c. dilute sulphuric acid. A part of the collected extractions is distilled with potassium hydrate to determine ammonia, and in another portion the soda is determined as sodium sulphate. This is obtained by evaporating the solution on a water-bath, volatilizing the sulphuric acid, and igniting the residue with additions of ammonium carbonate.

(e) Sulphuric acid. The sulphuric acid present in form of sulphate of ammonia or soda is determined by shaking the ethereal solution of the oils several times with small quantities of a saturated solution of salt, which is free from sulphuric acid. The collected, diluted and filtered extractions are precipitated with barium chloride. When an insight into the source of a turkey-red oil is desired, especially whether the substance in question is a castor oil turkey-red oil, the iodine number and acetyl number are taken of the total fats (a), to which, however, no stearic acid has been added.

An iodine number considerably under 70 and an acetyl number under 140 indicate admixture with other oils.

#### 4. Glycerin.

(a) Crude glycerin. For determination of glycerin in crude glycerin the acetin method is preferred. It depends on the phe-

nomenon that glycerin on boiling with acetic anhydride is quantitatively transformed into triacetin. If the latter be then dissolved in water, and the free acetic acid be neutralized with sodium hydrate, the dissolved triacetin can be saponified with caustic soda and the excess of the latter titrated back.

The necessary reagents are:

(a)  $\frac{1}{2}$  normal to normal hydrochloric acid accurately standardized.

(b) Dilute alkali, not standardized, which contains not more than 20 grs. sodium hydrate to the liter.

(c) Concentrated, about 10 per cent. alkali, best preserved in a flask provided with a 25 c.c. pipette. 1-1.5 grs. sample are weighed out in a wide-necked, small, round-bottom flask of about 100 c.c. capacity. 7-8 grs. acetic anhydride are added, with about 3 grs. dehydrated acetate of soda. The mass is boiled on a reflux for 1-1 $\frac{1}{2}$  hours. It is then allowed to cool somewhat, is diluted with 50 c.c. water, and likewise heated on a reflux until the oil is completely dissolved. The solution is now filtered into a 400-600 c.c. wide-necked flask. Usually a copious flocculent white precipitate remains on the filter. The solution is allowed to cool, phenolphthalein is added, after which it is neutralized exactly with dilute alkali. This is accomplished when the yellow color changes to reddish yellow. Dilute acid and cold solution must be used, as otherwise the triacetin will be saponified. 25 c.c. of the concentrated 10 per cent. alkali is then added from the pipette. The final adhering drops are counted the same for each experiment. It is boiled for a quarter of an hour and titrated back with hydrochloric acid. Exactly the same amount (25 c.c.) of alkali is then titrated with the hydrochloric acid, and from the difference the alkali used by the triacetin is found. This is then calculated into glycerin. (3 molecules NaOH represent 1 molecule glycerin.)

(d) Determination of glycerin in fats and soaps.

When glycerin in strongly alkaline solution is oxidized at ordinary temperature with potassium permanganate, it is completely transformed into oxalic acid:



On this reaction rests the method of Benedict and Zsigmondy, which will be described here in the modified form of Herbig and Mangold.

2-3 grs. fat are saponified in pure methyl alcohol with potassium hydrate. The alcohol is volatilized, the residual soap is dissolved in hot water and is decomposed with dilute hydrochloric acid. It is then heated until the separated fatty acids form a clear layer. To liquid fat some paraffin had best be added. It is cooled thoroughly, filtered off into a liter flask, and washed well. With soaps, the method described (p. 137) is followed up to this point. The solution is exactly neutralized with caustic potash and phenolphthalein. 10 grs. more caustic potash are added, and as much 5 per cent. potassium permanganate solution is added in the cold as would represent approximately  $1\frac{1}{2}$  times the theoretical amount. (For every part glycerin 6.87 parts potassium permanganate.)

The liquid will then no longer appear green, but blue or black. It is allowed to stand  $\frac{1}{2}$  hour at ordinary temperature. Hydrogen peroxide, in not too great an excess, is added, until the supernatant liquid becomes colorless. It is diluted to the mark, is shaken briskly, and 500 c.c. are filtered off through a dry filter. To decompose the hydrogen peroxide the liquid is boiled for  $\frac{1}{2}$  hour, cooled to about  $60^{\circ}$ , and after addition of sulphuric acid the oxalic acid formed is titrated with permanganate.

In place of filtration, the filtrate, after acidifying with acetic acid, may be precipitated with calcium chloride. When filtered it may be determined either gravimetrically by ignition to calcium oxide, or it may, after decomposition with sulphuric acid, be titrated with permanganate, as above.

# IX. Mordants and Tanning Materials.

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## A. Mordants.

THE substances which are most used for mordanting are compounds of aluminium, chromium, iron, tin, antimony and copper.

### 1. Alumina Mordants.

To these belong sulphate of aluminium, alum, sodium aluminate, aluminium acetate.

(a) Sulphate of aluminium  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$ . This is principally examined for iron and free sulphuric acid.

The qualitative test is the red color produced by a sulphocyanide of potassium solution. The latter is added to the solution of the sample, which has been oxidized with a little nitric acid. Lunge\* states that the method may be advantageously employed for the colorimetric determination of iron.

To conduct this there are necessary (a) a 10 per cent. potassium sulphocyanide solution, (b) pure ether, (c) an ammonium alum solution, containing 8.606 grs. iron alum and 6 c.c. pure conc. sulphuric acid to the liter. For the experiment 1 c.c. of this solution, diluted to 100 c.c., is used. This dilute solution contains .01 gr. iron in a liter, (d) pure nitric acid free from iron, (e) several cylinders for shaking. These are divided in  $\frac{1}{10}$  c.c. to 25 c.c., and should have about 5 c.c. free space above this. They should be nearly alike in height and diameter.

When small quantities of iron only are present, as is usually the case with good commercial material, 1-2 grs. of the aluminium sulphate under examination are dissolved in a little water and exactly 1 c.c. nitric acid (d) is added. The solution is heated, allowed to cool, and is diluted to 50 c.c. At the same time 1 c.c. nitric acid (d) is diluted alone to 50 c.c. with water. Exactly 5 c.c. alumin-

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\* Zeitschrift für angewandte Chem., Jahrg. 1894, p. 669, and 1896, p. 3.

ium sulphate solution in question are placed in one cylinder (*A*), and in the other cylinder (*B*) are placed 5 c.c. of the diluted nitric acid. A quantity, say 1 c.c., dilute iron solution ( $\gamma$ ) is added to the latter, and the same quantity of water is added to (*A*) in order to preserve the same dilution. Thereupon 5 c.c. sulphocyanide solution (*a*) are added to each cylinder, followed by 10 c.c. ether ( $\beta$ ), the stoppers are inserted, and the cylinders vigorously shaken until the aqueous layer has become colorless.

The intensity of the colors of the ethereal layers are thereupon compared. Rough differences can be instantly observed. At the same time, one or more tests are made with greater or smaller amounts of the diluted iron dilution. When shades are about alike, the comparisons are best made after standing a few hours. The accuracy can be easily brought to  $\pm .1$  c.c. iron alum solution, however, only when the total iron present is equivalent to the iron in 2 c.c. iron alum solution at the most. For the purpose of comparison, observation had best be made in transmitted light, preferably from above, through the entire column of ether. To this end the cylinder is placed on a white foundation. Should the sulphate of aluminium contain a large amount of iron, a considerably more dilute solution must be used for examination. When about  $\frac{1}{4}$  per cent. iron is present (the maximum amount allowed in use of the colorimetric method), only .2 gr. sample is dissolved in 250 c.c. 5 c.c. of this solution (= .004 gr. sample) are used in the experiment.

Free sulphuric acid is qualitatively tested for by treating the powdered and dried substance with 10 times its weight of absolute alcohol, whereby the free acid is extracted by the alcohol, in which it may be recognized by means of litmus paper. An approximate quantitative result is obtained by titration with  $\frac{1}{10}$  normal alkali. A frequently required exact quantitative estimation of the free sulphuric acid is made by dissolving 1-2 grs. aluminium sulphate in 5 c.c. water. 5 c.c. neutral saturated ammonium sulphate solution are added, and the mixture is stirred frequently during an interval of one quarter of an hour. Thereupon the entire aluminium sulphate is precipitated in the form of ammonium alum by the addition of 50 c.c. 95 per cent. alcohol, whereas the entire free sulphuric acid remains in solution. The solution is filtered. The residue is washed with 50 c.c. 95 per cent. alcohol, the filtrate is

evaporated on a water-bath, and the residue, dissolved in water, is titrated with  $\frac{1}{10}$  normal alkali.

(b) Alum. The examination for iron oxide and free sulphuric acid is conducted as in (a). Direct extraction of sulphuric acid with alcohol can, however, be resorted to in the latter determination. Large quantities of sodium alum can be detected in the presence of potassium alum by the greater solubility of the former in water. (Sodium alum dissolves in 2 parts water; potassium alum in 10 parts water.) Potassium alum  $K_2SO_4 \cdot Al_2(SO_4)_3 + 24 H_2O$  and sodium alum  $Na_2SO_4 \cdot Al_2(SO_4)_3 + 24 H_2O$  are principally used.

(c) Sodium aluminate. The examination according to Lunge was described in Chapter I., p. 17.

(d) Aluminium acetate. Alumina is determined in the usual manner. The estimation of acetic acid is made by distilling with phosphoric acid and titrating the distillate with normal alkali, using phenol-phthalein as indicator.

## 2. Chromium Mordants.

Potassium and sodium bichromates are most frequently used; the fluoride comes next, whereas chrome-alum is less frequently used.

(a) Potassium and sodium bichromates. In both materials the chromic acid is determined, as well as the sulphates, which frequently occur in sodium bichromate.

(a) Chromic acid. The estimation is conducted either volumetrically, preferably iodometrically, or gravimetrically, by precipitation with ammonia after the reduction of the chromic acid with hydrochloric acid and alcohol.

(b) Sulphuric acid. The solution reduced, as directed above, is precipitated with ammonia, and the sulphuric acid in the filtrate is precipitated with barium chloride.

In potassium bichromate the sulphuric acid is present as potassium sulphate, and in sodium bichromate as sodium sulphate.

(b) Fluoride of chromium. Chromium is determined by precipitation with ammonia.

(c) Chromium alum. As impurities it may contain organic matter, tarry matter, gypsum and sulphate of sodium in considerable quantities.

### 3. Iron Mordants.

These are used in form of ferrous and ferric mordants; in fact, as green vitriol in the first instance, and as ferric nitrate containing basic ferric sulphate, produced by the oxidation of the ferrous sulphate by nitric acid in the latter instance.

In both instances a determination of total iron is made by precipitation with ammonia after oxidation with nitric acid, and a determination of ferrous oxide by titration with permanganate in sulphuric acid solution.

In the ferric nitrate, furthermore, the sulphuric acid is estimated with chloride of barium after precipitation of the iron with ammonia and the nitric acid is estimated by the usual methods.

### 4. Tin Mordants.

Both stannous chloride (tin salt)  $\text{SnCl}_2 + 2\text{H}_2\text{O}$  and stannic chloride  $\text{SnCl}_4$  are used.

(a) Stannous chloride. Pure tin salt dissolves completely in 5 times its weight of absolute alcohol; the oxidized salt gives a fine pulverous or flocculent precipitate, which dissolves on addition of alcoholic hydrochloric acid. Adulterants remain in the form of crystalline fragments.

Stannous oxide (stannous chloride). Method of Goppelsoder and Trechsel, modified by Fraenkel.\*

3-4 grs. tin salt are dissolved in 30-40 c.c. 10 per cent. hydrochloric acid and diluted to 500 c.c. 50 c.c. solution and 50 c.c. one-tenth normal potassium bichromate solution are placed in a stoppered flask, and after 15 minutes 10-15 c.c. potassium iodide solution and 5-10 c.c. hydrochloric acid (both 1 : 10) are added. After a half-hour action it is diluted with about 200 c.c. water, and the precipitated iodine is titrated back with one-tenth normal hyposulphite solution. The stannous salt is calculated from the difference in c.c. between the bichromate added and the hyposulphite used in back titration.  $1 \text{ SnCl}_2 = 1 \text{ SnO} = 2 \text{ I}$ . When exactly one-tenth normal solutions are used, the difference need only be multiplied by .01125 and calculated into per cent. in order to obtain the amount of crystallized tin chloride present. ( $\text{SnCl}_2 + 2 \text{ H}_2\text{O}$ .)

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\* Contribution from the K. K. tech. Gewerbe-Museum, 1892. Volume 7.

(b) Tin chloride. This comes into the market in solid form or in form of solutions containing 10-20 per cent. tin. It is to be tested particularly for iron and nitric acid. Stannous chloride is detected by means of mercuric chloride. Total tin, .5-1 gr. salt or 2-4 c.c. solution are diluted to 100-200 c.c. with water, and in case stannous chloride is present a weak iodine solution is added to yellow coloration. Ammonia is then added until the solution faintly opalesces, after which the tin is precipitated with an excess of a saturated solution of Glauber salt. The liquid is heated to boiling for a while and the voluminous precipitate is decanted several times with hot water. It is then thrown on a filter, is thoroughly washed, ignited, and weighed as tin oxide.

### **5. Antimony Mordants.**

Chiefly to be considered are: Tartar emetic (potassium antimonyl tartrate)  $K_2SbO_3 \cdot C_4H_4O_6 + \frac{1}{2}H_2O$  and De Haen's salt  $SbF_3 \cdot (NH_4)_2SO_4$ . The potassium antimony oxalate has been used very little recently.

An antimony determination suffices as a rule. This is conducted gravimetrically in the usual manner by precipitation with hydrogen sulphide. A volumetric method consists of titration with iodine solution: .5 gr. sample is dissolved in about 50 c.c. water and made slightly alkaline with bicarbonate of soda solution. A precipitate which might form is removed by addition of Seignette salt. Starch paste is then added to the solution, which is titrated until a blue color of short duration is formed ( $1 Sb_2O_3 = 4 I$ ). The acids present are best determined after precipitation of the antimony with hydrogen sulphide. Oxalic acid is recognized by the precipitate in acetic acid solution by calcium chloride.

### **6. Copper Mordants.**

Blue vitriol is principally used, and sometimes copper acetate. The copper is estimated in the usual manner. Iron should be tested for qualitatively and its quantity estimated.

## **B. Tanning Materials.**

Chemically, tanning substances are not yet sufficiently understood to allow of their precipitation in isolated conditions or in the form of characteristic compounds. In consequence, the customary methods cannot be claimed to be exactly scientific.

Practically they yield approximate satisfactory results, providing that the material present which tans is designated as the tanning substance; that is, those organic substances which are absorbed from their solutions by the hide. Hereby a number of different chemical substances under the general name of "Tanning Substance" are usually determined.

Of the customary methods, the procedure of Simand and Weiss, of the Vienna Experimental Station, will be described. This has recently become popular. According to these chemists a portion of the solution containing tannin is evaporated and the constituents soluble in hot water are then weighed. In another portion the non-tannins, soluble in hot water, are estimated by evaporating the solution from which the tannins have been withdrawn by hide powder. The remaining substance is found from the difference.

### 1. Tannin Extracts.

(a) Water and ash. 2-3 grs. extract are evaporated, if necessary, in a platinum dish, and are dried to constant weight at 100°. The loss of weight represents water. The residue is ignited and weighed as ash.

(b) Matter soluble in hot water. A weighed amount of the extract containing at least 10-12 grs. of the dry material is dissolved in water, placed in a liter flask, and upon cooling is diluted to the mark and filtered. 100 c.c. clear filtrate are evaporated in a weighed platinum dish, are dried to constant weight at 100°, and weighed. The residue is ignited, the ash is deducted, and the difference is considered as soluble organic matter (tanning substances and non-tanning substances).

(c) Organic matter insoluble in hot water. If the percentages of ash, water and organic matter soluble in water found as in (a) and (b) are deducted from 100, the organic matter insoluble in hot water is obtained.

(d) Non-tannins. A tube 2-2.5 cm. wide, 12 cm. high, not too thin, open at both ends and possessing rounded edges, is closed at the lower end with a cork, which should not extend too far into the tube. This is charged with 6 grs. hide powder in such a way as to be evenly distributed without the presence of any marked gaps at the walls. The tube, as prepared, which should still possess an

empty space 3 cm. high above the powder, is placed in a beaker 13-14 cm. high and 5 cm. wide. The beaker is gradually filled with the solution prepared as in (*b*), without allowing the solution to touch the powder from above. After a few hours the solution will have risen from below in the inner tube, above the surface of the hide powder. By means of a tight-fitting rubber stopper, containing one perforation, a siphon filled with water (described below) is inserted in such a way in the upper part of the tube containing hide powder as to dip into the liquid, but somewhat above the upper surface of the hide powder. The liquid, now clear, is gradually drawn off. The first 30 c.c. liquid are discarded. The following 100 c.c. are evaporated and dried to constant weight. If the ash be deducted from the resulting residue, the difference gives the non-tanning matter.

The siphon previously referred to is a glass tube twice bent at right angles, one arm of which is short and is placed in the tube containing the hide powder, whereas the other is twice the length of the tube containing the powder and extends downwards. The horizontal part of the tube is about 4 cm. long.

(*e*) Tanning substances. They are determined by deducting the non-tanning substances (*d*) from the matter soluble in hot water (*b*).

## 2. Raw Products.

In order to make the above described methods applicable to raw products used in tanning (barks, wood, etc.), a solution containing 1-1.2 grs. dry material in 100 c.c. is prepared by exhausting the material in question with water.

For extraction the following apparatus (Fig. 12) was prepared by the Vienna Experimental Station. *A* is a wide-mouth flask of more than 1 liter capacity. In this the mantle *B* is inserted through a hole in the stopper. The former is made of sheet copper, which is tin-plated.

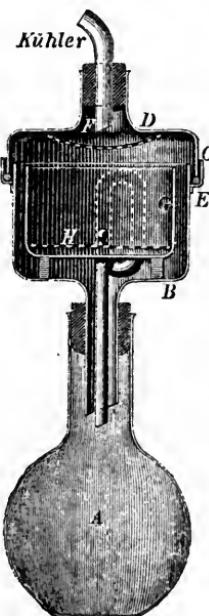


FIG. 12.—Extraction Apparatus for Tanning Materials.

On the upper end a low copper ring *C* is joined, and in the trough so formed is fitted the sheet copper, tin-plated, cover, *D*. A rubber ring, *E*, set in the trough, and two diametrically opposite bayonette clasps, serve to make the jacket steam-tight when the cover is adjusted. The cover is closed by a cork stopper, through which a fairly wide tube issues to a condenser. Inside the cover a tin plate is soldered, which is depressed somewhat toward the center, and which is provided with pea-sized perforations, so that the condensed water-drops are equally distributed. In the space formed inside of the jacket and lid the vessel *G* is placed as a receptacle for the material. This, as well as the siphon, issuing from an opening in the bottom, and the perforated floor *H*, is made of tin.

The vessel *G* is sufficiently large to conveniently hold the necessary quantity of material to be extracted. According to Eitner, Weiss and Anderen, of pine and oak bark, quebracho wood, etc., 50-60 grs. should be extracted; of gall nuts, valonia, etc., 20-25 grs. should be extracted.

A similar apparatus, but made of glass, was also prepared by the Vienna Station. Both forms are obtainable from Stefan Baumann, Vienna, VIII, Florianigasse 11.

The examination of the extract so obtained is conducted in exactly the same manner as that described under tanning extracts. The objection made to the above procedure is that the concentrated solutions prepared in the heat precipitate difficultly soluble tannin upon cooling, thereby causing loss. A method based on a similar principle, in which, however, much more dilute solutions are used, has been perfected by v. Schroeder. As far as we know the Vienna method is at present the most popular, and among other countries it is practiced in England.

## X. Textile and Dyeing Industries.

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THIS section embraces a large number of raw materials and substances used technically, which may be arranged in the following groups: Textile fabrics, bleaching materials, wool-oiling material, thickening material, dressing and finishing materials, tanning materials, mordants and dyes. Some of these groups, such as wool-oiling material, tannins and mordants, have already been treated of in previous chapters.

Others are brought into commerce in so many different forms and kinds that only a few instances will have to suffice.

### 1. Textile Fibers.

The best means of distinguishing the textile fibers is the microscope, for the use of which reference only will be made to the excellent little work of v. Höhnel.\* The chemical points of difference between animal and vegetable fibers are:

(α) Behavior when burned. When animal fibers are burned they disseminate the peculiar odor of burning nitrogenous matter. They burn much slower than vegetable fiber.

The former leave a voluminous, difficultly combustible coke, and the latter incinerate easily and completely.

(β) Behavior toward alkalies. Boiling with a 10 per cent. solution of potassium or sodium hydrate dissolves animal fibers, whereas vegetable fibers remain practically unattacked.

(γ) Behavior toward acid. After treatment for 2-3 hours with dilute acid, especially sulphuric acid (sp. gr. 1.03-1.04), and subsequent drying at about 100°, vegetable fibers are destroyed (carbonized), while animal fibers are scarcely attacked.

Chloride of magnesium and chloride of aluminium solutions which give off acid above 100° react similarly.

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\* Die Microscopie der technisch verwendeten Faserstoffe von F. v. Höhnel, Wien, 1887.

(d) Behavior toward nitrating mixture. According to Peltier, the fibers under examination are immersed for about  $\frac{1}{4}$  hour in a mixture of equal volumes conc. sulphuric acid and conc. nitric acid, after which they are washed with much water. Silk is thereby completely dissolved, wool is colored yellow or light brown, whereas vegetable fibers change neither in color nor structure, but yield highly combustible gun-cotton when dried.

(a) Half-Woolen Yarns and Fabrics.

Moisture, fat and cotton are determined in these, and the wool is obtained by difference.

(a) Moisture. About 10 grs., if necessary, more, are dried at  $100^{\circ}$  to constant weight.

( $\beta$ ) Fat. The sample dried according to (a) is extracted in a suitable apparatus with ether. The ethereal solution, filtered, if necessary, is placed in a weighed flask, the ether is distilled off, and the last traces are removed by a current of air until a nearly constant weight is obtained. The fat so obtained may, if necessary, be tested for saponifiable and unsaponifiable constituents. Soaps, if present, do not dissolve in the ether. They may be determined by extraction with alcohol subsequent to the extraction with ether.

( $\gamma$ ) Cotton. The dried sample, freed from fat, is placed in a boiling-hot 10 per cent. solution of caustic potash; the boiling is continued for 15 minutes, when the whole is poured into a beaker filled with distilled water. The remaining cotton is removed, wrung out, well washed, and finally dried at  $100^{\circ}$  to constant weight.

(d) Sheep's wool is estimated by the difference reckoned on 100.

(b) Half-Silk.

In fabrics containing silk and cotton, the cotton can be estimated by the method described under ( $a$ ,  $\gamma$ ).

(c) Shoddy.

This consists of a mixture of unused wool fibers and more or less already used fibers, which sometimes contain cotton.

To determine the animal fibers, shoddy, like half-wool, is subjected to the alkali treatment. Microscopically, shoddy can be detected by the fact that, while in the main it consists of uniformly col-

ored fibers, other differently colored fibers are present, which shows that a uniform dyeing process was not used. Besides this, innumerable gaps, as well as wool fibers of very different character, can usually be detected in shoddy. A separation of the different fibers present, and these, with an approximate idea of the relation of one to the other, can also be conducted with the microscope, but requires considerable practice.\*

(d) **Oxycellulose.**

This is formed by the action of many oxydizing agents, such as chlorine, bleaching lime, hydrogen peroxide, potassium permanganate, and chromic acid on cotton, and can, therefore, frequently arise in the bleaching process. Its production must be carefully avoided on account of the consequent weakening of the cotton fiber, which becomes especially evident in the subsequent treatment with alkalies, soda or soap.

The property of oxycellulose of absorbing basic dye can be made use of as a test, according to Witz. The cotton to be tested is placed in a  $\frac{1}{2}$  per cent. solution of methylene blue. Those portions which are changed to oxycellulose are colored more or less blue. Better than this method is the power of oxycellulose to reduce Fehling's solution. For this purpose, the fabric,† which is prepared by repeated boiling with water, or, better, by digesting with malt infusion at  $65^{\circ}$ , is boiled for 5 minutes, stirring constantly with a mixture of equal parts Fehling's solution, to which an equal volume of water has been added. Thereupon the fabric is washed. Those parts containing oxycellulose are recognized by the rose color which arises from deposited cuprous oxide. This becomes more intense the more oxycellulose is present in the fabric.

The yellow color produced on oxycellulose spots by warming the fabric with alkaline  $\beta$ -naphthol solution can be used as a test. However, this reaction is less sensitive.

**2. Bleaching Materials.**

Sulphurous acid, sodium bisulphite and hydrogen peroxide are principally used to bleach animal fibers. Beside these, chloride of lime

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\* See Dr. F. R. v. Höhnel. Die Microscopie der technisch verwendeten Faserstoffe, Wien.

† Starch especially is often difficult to remove.

is used in bleaching vegetable fibers. It is taken for granted that the examination of all these substances is known.\* Recently salts of persulphuric acid (persulphates) have been used as bleaching agents. The bleaching action depends on their strongly oxidizing properties. The following reaction of decomposition of the ammonium salts demonstrates this :



The estimation of the active oxygen, according to Ulzer, is conducted as follows :†

About .3 gr. sample is decomposed by addition of an excess of ferrous ammonium sulphate solution (1-1.5 grs.) and dilute sulphuric acid. The solution is boiled for  $\frac{1}{2}$  hour in a current of carbonic acid or in a flask provided with a Bunsen valve, and the excess of ferrous salt is titrated back with permanganate. From the ferrous ammonium sulphate oxidized, the active oxygen can be calculated, and from this, by the above equation, the persulphate is found.

Ammonium persulphate is the common form.

### 3. Sizing Materials.

These serve on the one hand for the preparation of dressings, on the other hand for the laying on of coloring matter in calico printing. The different kinds of starch and flour, dextrin, gums, tragacanth, albumin, casein, and many others, are used. The investigation of these products is often difficult and uncertain. Starch, dextrin and a few reactions for gums only will be described.

#### (a) Starch.

The chemical examination of starch has already been described in Chapter VI. Microscopic means are employed to distinguish between the different varieties.

#### (b) Dextrin.

Dextrin is obtained by the action of dilute acids on starch at high temperature, also by heating *per se*; and it contains, in addition, water, ash, maltose, starch, and other organic substances. The determinations of these constituents, as well as the acidity, are conducted according to Hanofsky as follows :

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\* Contribution from the K. K. tech. Gewerbe-Museum, Jhrg. 1895, p. 310.

† See Appendix.

25 grs. dextrin are placed in a flask of 500 c.c. capacity and are well shaken with cold water, filled to the mark, allowed to settle, and are filtered through a ribbed filter. In the filtrate, maltose, dextrin and acidity are determined.

( $\alpha$ ) Maltose. This is determined by the cuprous oxide, which it has the power to precipitate from Fehling's solution.

Since the power of reduction changes with the concentration, the latter must be made the same always. A test is made, therefore (similar to that of invert sugar, p. 85,), to determine how much of the solution is required to reduce 10 c.c. Fehling's solution. In the actual determination 1-2 c.c. less are taken, and are diluted with sufficient water to bring the total volume to 57-58 c.c. The liquid is run into a porcelain dish in which 10 c.c. Fehling's solution have previously been placed. It is heated to boiling, and is kept in that state exactly 4 minutes. The precipitated cuprous oxide is thrown on the asbestos filter, and is treated further in the usual manner. Using the concentration referred to, 113 copper = 100 anhydrous maltose, the percentage of maltose so found = M.

( $\beta$ ) Dextrin. 50 c.c. solution are diluted to 200 c.c., and are heated to incipient boiling on a reflux with 15 c.c. hydrochloric acid (sp. gr. 1.125) for two hours. Dextrin and maltose are thereby changed to dextrose, the solution is filtered into a 500 c.c. flask, is nearly neutralized with caustic soda, and diluted to the mark. The dextrose in 25 c.c. is determined with Fehling's solution. If the dextrose in per cent. = D, the dextrin will be

$$.9 (D - 1.05 M),$$

since 20 parts dextrose correspond to 19 parts maltose.

( $\gamma$ ) Acidity. 50 c.c. solution are titrated with one-tenth normal alkali, using phenol-phthalein as indicator. The quantity of one-tenth normal alkali calculated in 100 grs. substance is designated the acidity.

( $\delta$ ) Starch. 2.5-3 grs. dextrin are mixed with 200 c.c. water and are treated with 15 c.c. hydrochloric acid (sp. gr. 1.125), as in ( $\beta$ ). The solution is nearly neutralized, diluted to 500 c.c., and likewise treated for the dextrose in 25 c.c. Maltose, dextrin and starch are converted into dextrose. If the percentage of dextrose = D, then the percentage of starch will be

$$.9 (D_1 - D).$$

(7) Water and ash are determined in the usual manner. If the water = W per cent. and the ash A per cent., the "other organic constituents" present will be

$$100 - (\text{Maltose} + \text{Dextrin} + \text{Starch} + W + A).$$

(c) Gums.

Of the many kinds of gums, gum arabic, gum Senegal and gum tragacanth are chiefly used.

These three varieties can be distinguished in pure condition by their appearance. Gum arabic is more easily, gum Senegal less readily soluble in water, whereas gum tragacanth is scarcely soluble at all, but swells up to a slimy mass, which distributes itself throughout a sufficient quantity of water. Gums are frequently adulterated with dextrin.

Lieberman has proposed the following tests for the detection of gum Senegal and dextrin in gum arabic. The gum is dissolved in hot water, treated with an excess of caustic potash and some copper sulphate, slightly warmed and filtered. The milky filtrate is boiled. A perceptible precipitate of cuprous oxide indicates the presence of dextrin.

The precipitate formed by the action of caustic potash in the copper sulphate, and which contains the gum acids, is washed with water, dissolved in dilute hydrochloric acid, and precipitated with alcohol. It is allowed to settle for  $\frac{1}{2}$ -1 day, when the supernatant liquid is poured off. The precipitated gum in the vessel is washed with alcohol, dissolved in hot water, and to it are added an excess of caustic potash and some copper sulphate. A balled-together precipitate, quickly ascending to the surface, indicates gum arabic, whereas a more divided, fine flocculent precipitate discloses gum Senegal or an admixture of the same. In the first instance, in addition, an aqueous solution, boiled with caustic potash, should turn amber yellow. If the amber color arise in the second case under the same conditions a mixture of Senegal gum and gum arabic is present, whereas a faint yellow or no color indicates Senegal gum alone.

**4. Finishing Materials.**

The number of substances used for dressings is very large and is on the increase. In consequence only the most important will be

selected, and the part which they play in finishing will be mentioned.

(α) Sizing material. These were treated of in the previous chapter.

(β) Substances which make the goods soft, pliable and hygroscopic : Glycerin, grape sugar, fats, tallow, stearin, paraffin, cocoanut oil, wax, ozokerite, calcium chloride, zinc chloride, sodium and ammonium salts.

(γ) Loading materials. Gypsum, chalk, barium sulphate (permanent white), sulphate of magnesium, sodium and zinc, talc, china clay, magnesium chloride, barium chloride, barium carbonate, lead sulphate.

(δ) Coloring matters. Ultramarine blue, Berlin blue, indigo blue, indigo carmine, all kinds of blue cotton-dyes, ammoniacal cochineal, black, gray and brown mineral pigments.

(η) Antiseptics. Phenol, creosote, salicylic acid, tannin, camphor, oxalic acid, zinc salts, boracic acid, borax, alums, aluminium sulphate, formic acid, etc.

(ε) Water-proof materials. Fats, varnishes, resins, paraffin, tannin, basic aluminium acetate and aluminium soaps. Besides these there may be contained materials which render the fabric fire-proof, such as boric acid, phosphates, silicates, etc., and such as impart metallic lustre to the goods: metallic sulphides, metal-dust, etc.

With this array of substances no general method of investigation of finishing materials can be given.

In the following, the analysis of two simple, frequently occurring products are described :

(α) Finishing material containing starch paste and chloride of magnesium.

(α) Starch. 10-20 grs. material are heated for three hours to incipient boiling in a 500 c.c. flask with 200 c.c. water and 20 c.c. hydrochloric acid (sp. gr. 1.125). To avoid evaporation of the water a reflux is used. Upon cooling, the contents are poured into a 500 c.c. measuring-flask, and an excess of caustic soda is added to precipitate all the magnesia capable of precipitation by alkali. The solution is filled to the mark and is rapidly filtered through a dry filter. In 25 c.c. filtrate the dextrose formed by inversion is

estimated by means of Fehling's solution, as is described under starch (p. 99).

(β) Magnesia and chlorine. The determination of these constituents in the ash is not possible on account of the easy decomposition of magnesium chloride. The presence of starch likewise interferes with the precipitation. The latter is therefore inverted with dilute nitric acid as in (α) and in one portion the chlorine, and in another portion the magnesia are determined by the usual methods.

(γ) Water and ash. An exact determination of these constituents cannot be accomplished on account of the easy decomposition of magnesium chloride and the tenacity with which water adheres. Nevertheless, approximate results can be obtained by drying a weighed portion at about 100° to almost constant weight and incinerating the residue. The water of crystallization of magnesium chloride is for the greater part still present after drying.

(δ) Finishing material, containing starch paste, fat and sulphate of zinc.

(α) Starch, zinc oxide and sulphuric acid. 10-20 grs. material are inverted as before with hydrochloric acid, separated from the fat by filtration through a moistened filter, and diluted to 500 c.c., after approximate neutralization with caustic soda. The starch is determined as before in 25 c.c. of this solution. Other measured portions are used for the determinations of zinc oxide and sulphuric acid by the usual methods.

(β) Fat. Since the fat separated in (α) does not usually answer for further examination, a larger portion of the finishing material is preferably taken. It is inverted with hydrochloric acid, and the separated fat is extracted repeatedly by shaking with ether. The collected ethereal extractions are freed from ether by distillation and the last portions of the solvent are removed by a current of air, after which the residue is weighed. It contains the total fat. In the latter, the usual constants, such as saponification number, iodine number, etc., can be determined in addition to unsaponifiable portions of the fat. The nature of the latter is thus ascertained.

### 5. Dye-Stuffs.

These are divided into natural and artificial dye stuffs, according to their origin. According to their use, they may be divided into basic, acid, mordant and direct cotton dye-stuffs.

To these are added a number of dye-stuffs formed directly on the fiber, such as "vat" dyes, diazotized dyes and aniline black. Each of these groups represents a special dyeing process, which will be briefly discussed here.

*Basic dyes, applied to cotton.*—The material to be dyed must first be mordanted. Mordanting is usually conducted in the following manner: The cotton is first placed in a bath of tannin at 60° for about 12 hours, after which it is thoroughly wrung out and placed in a bath of tartar emetic, 10–20 grs. per liter, or the corresponding amount of antimony salt [SbF<sub>3</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]. Thereupon it is washed well and dyed in the bath containing the dye at a temperature of 50–60° until the bath is exhausted.

*Applied to wool.*—Takes place in a bath which is either neutral or slightly acidified with acetic acid. The bath is gradually heated to boiling.

*Applied to silk.*—Takes place in neutral, slightly acid (acetic) or separate soap bath, with gradually heating to about 70°.

Among the basic dyes belong fuchsin, auramin, malachite green, victoria blue, methyl violet, etc.

*Acid dyes* find use chiefly in dyeing wool. Dyeing is conducted in a bath containing 2–4 per cent. sulphuric acid, or 2–5 per cent. sulphuric acid and 10–15 per cent. Glauber salt, or 5–10 per cent. sodium bisulphate. A gradual rise in temperature and eventually continuous boiling are required.

The group of basic dyes is very extended. There may be mentioned, for instance: Ponceau, naphthol black, alkali blue, patent blue, acid fuchsin, acid violet.

*Mordant dye-stuffs.*—The dyeing of cotton as well as of wool requires previous mordanting. Aluminium, chromium and iron mordants are chiefly used. Mordanting wool is accomplished by boiling 1–2 hours in the solution of the mordant (3–4 per cent. potassium bichromate, 6–10 per cent. aluminium sulphate, 4–6 per cent. ferrous sulphate) with the addition of sulphuric acid (1 per cent.), acid potassium tartrate (3–8 per cent.), or oxalic acid (1–2 per cent).\*

Cotton mordanting must be accomplished by an artificial fixation

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\* Recently lactic acid has also found use.

with chemical precipitants. The cotton is first placed in a fairly strong solution of the mordant (aluminium sulphate, aluminium acetate, chrome alum, chromium fluoride, ferric nitrate). It is then pressed out and passed through a bath containing soda, chalk, ammonium carbonate, etc. Finally it is well washed.

Iron and tin baths are used mostly for silk. As a rule, a simultaneous "weighting" occurs, and sometimes also the silk becomes colored, as, for instance, with acetate of iron and tannin. In such cases the operation must be repeated several times.

Dyeing mordanted goods is conducted in neutral baths. On account of the insolubility of many mordant dyes, the bath must be kept in motion during the process of dyeing. Also, in order to insure uniform dyeing, the temperature must increase very slowly. To the mordant dyes belong the large group of alizarin dyes and most of the natural dye-stuffs, blue wood, yellow wood, red wood, cochineal, etc.

*Direct cotton dye-stuffs.* (Benzidine colors also dye vegetable fibers directly.) Dyeing is usually conducted in weak alkaline baths (soda, soap, 2-5 per cent.; borax, sodium aluminate, 5-10 per cent., and sometimes in neutral, salt, Glauber salt, or weakly acid baths). The operation usually takes place at a boiling temperature. This group is also very large. To it belong, among others, benzopurpurin, chrysamin, benzoazurin, diamine blue, diamine black.

"*Vat*" dyeing is almost exclusively conducted with indigo.\* The insoluble indigo blue or indigotin contained therein must first be transformed in the vat into soluble indigo white. Reducing agents mostly used are ferrous sulphate (iron vat), zinc dust (zinc vat), hyposulphurous acid (hydrosulphite vat). The fabric impregnated with indigo white is rapidly colored blue by oxidation in the air.

*Diazotized dyes.*—Benzidine dye-stuffs can be diazotized in the fiber and developed in a bath containing dissolved phenols, naphthols or amines. A new color is formed which is similar to the original, but more perfect, and which is distinguished for its fastness. The developers mostly used are phenol, resorcin,  $\beta$ -naphthol,

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\* Recently the artificially prepared indophenol has come into use.

m. phenylenediamine, naphthylamine ethers, amido diphenylamine, and others. The colors produced are also called ingrain or developed colors. As an example, the diazotizing of primuline, first attempted, may be mentioned. The goods are dyed as usual at first. They are then washed and placed in a diazotizing bath containing in 200 parts water 1 part sodium nitrite and the requisite quantity of sulphuric or hydrochloric acid (sulphuric acid, about twice as much, and hydrochloric acid, about three times as much as the quantity of sodium nitrite). The diazotizing bath is kept cool by addition of ice. After short immersion, the goods are rinsed in cold water and are placed in the developing bath. This may consist of an alkaline solution of phenol, resorcin,  $\beta$ -naphthol, a solution of m. phenylaminenediamine hydrochloride, etc. The developing bath is usually kept cold. The goods are subsequently rinsed.

Somewhat different from this is the production of insoluble azo dye-stuffs on fiber which has not been previously dyed.

The colors so produced are termed "ice colors." They are prepared for dyeing, especially for the printing, of cotton goods. The goods to be dyed are first impregnated with an alkaline solution of  $\alpha$ -naphthol, and are then drawn through a diazo solution. In this manner there is produced in the filter an azo dye-stuff which is quite fast toward water and very fast toward acid and alkali. As an example, the production of the very beautiful paranitraniline red may be mentioned. 144 grs.  $\beta$ -naphthol are dissolved in 10 liters water, and 145 grs. caustic soda (sp. gr. 1.333), with addition of 500 grs. turkey-red oil. The goods are impregnated with this solution and dried. They are afterwards placed in the diazotizing bath. The latter is obtained by dissolving in a boiling solution of 69 grs. paranitraniline in 200 c.c. hydrochloric acid and 200 c.c. water. To the cooled solution 1 liter cold water, and, after thorough cooling, 500 grs. ice are added. It is then diazotized with 250 c.c. twice normal nitrite solution, is diluted to 10 liters and treated with 300 grs. sodium acetate before using. The goods, which are removed from the diazotizing bath, are well rinsed, slightly soaped at 40°, and dried.

*Aniline black* is a dye-stuff which is formed on the fiber by the oxidation of aniline. Potassium bichromate or chlorate are usually used as oxidizers. It can be produced on cotton, wool or silk.

**Method of Testing.**

The best means of determining the value and strength of a dye-stuff is by comparative dye tests. To this end a "type" or standard sample may be employed for comparison; or, when a choice is to be made between several kinds of the same dye, the process may be undertaken with all the samples. In the first case dyeing is conducted under the same condition until the same shade is obtained, and a comparison is made between the amounts of dye used. They are merely proportional to the value of the dye-stuff. In the second case dyeing is conducted with dyes in quantity of equal price and the colors produced are compared. A process of dyeing is selected which is as simple as possible, and which gives reliable value for the strength of the dye and the clearness of the shade. In order, for instance, to avoid mordanting the cotton, wool may be used with basic dyes. The quantity of mordant is rather taken somewhat higher than required in actual practice when mordant dyes are used. Wool is mordanted in the manner previously mentioned. Strips of cotton calico\* printed with iron and aluminium mordants are preferably used instead of cotton. The quality of dye chosen should not be too large, because lighter shades are more easily compared. In case the bath is not exhausted, a second, and, if necessary, a third sample is placed in the same, until exhaustion is complete.

The samples to be dyed should possess equal weight, and for carded wool, cotton yarns or calico, should equal about 10 grs. If necessary, they are first mordanted and dyed in porcelain or glass vessels. In order to preserve uniform heat, the vessel is placed in an oil- or glycerin-bath. The quantity of water used is about 50 times the weight of the goods when these are wool, and 30 times the weight when cotton is used. The evaporated water is replaced from time to time. To prepare the dye-stuff solution, 1 gr. per liter of coal-tar colors is used, and 10-20 grs. dye-wood extracts per liter. 10-20 grs. insoluble dye-pastes are weighed off, mixed with one liter water, and thoroughly shaken before using. The dye-stuff solution is added from a burette or pipette and manipulated as previously stated. After dyeing, the goods are washed, and, if necessary, soaped. If, for example, in one case 70 c.c., in another

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\* These may be readily purchased.

56 c.c. of two solutions containing blue wood extract (in both cases 10 grs. extract per liter) were used, their value will be the reverse : 56 : 70 or 80 : 100.

*Tests for impurities.*—Inorganic admixtures are easily recognized by the increased ash. The nature of these is determined in the examination of the latter. Organic impurities, such as starch and dextrin, remain behind on extraction with alcohol in many cases, and can thus be determined quantitatively.

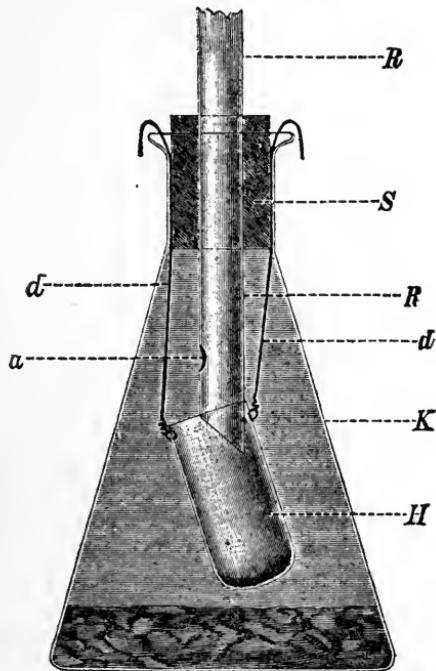


FIG. 13.—Indigo Extraction Apparatus.

#### Special Methods of Investigation.

Special methods of investigation are also applied, in addition to the dye tests, to certain natural dye-stuffs. Of these the examination of indigo for indigotin, according to Schneider, will be mentioned. This depends on the solubility of indigotin in naphthalene. 30–50 grs. pure naphthalene, which has been previously melted to expel water, are placed in the Erlenmeyer flask, *K*, of the accompanying apparatus (Fig. 13). The Erlenmeyer flask may be replaced by a wide-necked test-tube.

Thereupon about .3 gr. of air-dried indigo is placed in the extraction capsule *H* (these are for sale by Schleicher and Schüll), mixed with ignited bar-sand by means of a spatula, or by shaking, and covered with a small paper plate. It is then hung in the flask by two wires which are inserted into the sides of the capsule. The wires are pressed against the inner walls by the cork *S*. Through a hole in the latter there is placed a condenser-tube *R*, provided with a slanting end extending into the capsule, and which may have an opening at *a* in order to facilitate the issue of the naphthalene vapors. This is not indispensable, however. The naphthalene is now gradually brought to boiling, when the vapors, which are condensed in the tube, drop into the capsule and extract the indigotin.\* Any solidified naphthalene in the tube may be removed by heating. Heat is applied until the naphthalene which flows from the capsule remains nearly colorless for a time. It is then allowed to cool, the contents of the flask are covered with ether, and after all soluble matter has gone into solution the residue is thrown on a dried and weighed filter, is well washed with ether, dried at 100° and weighed as indigotin. In a separate portion of the sample the water is determined by drying at 100°, and the ash is determined by first subliming off the indigotin with a small flame and afterwards igniting briskly to constant weight.

#### Recognition of Dye-stuffs.

The behavior of the dye-stuff with acids, alkalies and reducing agents serves as a means of identification. The reactions bearing on this, most of which depend on changes of color and decolorization, and which can also be used to identify a dye on the fiber, are specially treated of in the excellent work of G. Schultze and P. Julius, *i.e.*, "Tabellarische Uebersicht der künstlichen organischen Farbstoffe." A detailed description at this point would be too extensive.

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\* Indigo red is also extracted by naphthalene, but on subsequent treatment with ether it dissolves, while indigo-blue remains undissolved.

# XI. Products of the Coal-Tar Industry.

## I. Crude Benzene.

### (a) DETERMINATION of petroleum hydrocarbons.

100 grs. crude benzene are nitrated with a mixture of 150 grs. nitric acid ( $42^{\circ}$ , Bé.) and 220 grs. concentrated sulphuric acid. The product obtained is carefully washed with water and very dilute alkali, after which it is dried and subjected to fractional distillation. The petroleum hydrocarbons, which distil up to  $150^{\circ}$ , are measured.

(b) Fractional distillation. 100 c.c. crude benzene are placed in a distilling bulb in which a thermometer is placed in such a manner that the upper end of the mercury reservoir is parallel with the lower point of contact of the exit tube. Connected with the distilling bulb is a condenser, at the end of which a measuring cylinder is placed. Heat is now gently applied, and the temperature at which the first drop goes over is recorded as the beginning of boiling. Distillation is continued rapidly and yet in such a manner that the drops may be counted as they run into a cylinder. The volume of the distilled fluid is read off every  $5^{\circ}$ . At  $100^{\circ}$  the flame is removed, the tube is allowed to drain, and the volume of the distillate is recorded. Thereupon distillation is continued until complete.

The following table shows the course of distillation of 90, 50 and 30 per cent. benzene :

Benzene.	Starting Point.	Amount Distilled in c.c. up to							Specific Grav.
		$85^{\circ}$	$90^{\circ}$	$95^{\circ}$	$100^{\circ}$	$105^{\circ}$	$115^{\circ}$	$120^{\circ}$	
90 per cent.	$82^{\circ}$	20	72	84	90	95	98	...	.882
50 " "	$88^{\circ}$	...	5	30	50	64	81	94	.880
30 " "	.....	...	2	12	30	42	92	90	.875

## 2. Crude XyloL.

*Determination of the three xyloLs according to Lewinstein.*—The method, which is little used, practically depends on the difference

in behavior of these substances with dilute nitric acid, and, furthermore, with conc. and fuming sulphuric acid.

100 c.c. crude xylol are boiled, while constantly agitated, with 40 c.c. nitric acid (sp. gr. 1.4) and 60 c.c. water for  $\frac{1}{2}$ -1 hour. As soon as the evolution of red fumes has ceased, the acid is separated from the hydrocarbons in a separatory funnel. The latter are washed with dilute alkali and distilled in a current of steam.

The solution of the hydrocarbons (*a*) in the distillate, consisting of metaxylol and hydrocarbons of the fatty series, is measured and thereupon shaken for a half-hour with  $1\frac{1}{2}$  times the volume conc. sulphuric acid. Metaxylol is thereby dissolved as sulphonic acid, whereas the aliphatic hydrocarbons remain. If their volume (*b*) be deducted from the previous volume (*a*), the difference (*a*-*b*) will equal the metaxylol present.

To determine the paraxylol, 100 c.c. crude xylol are shaken for half an hour with 120 c.c. conc. sulphuric acid. Ortho- and metaxylol dissolve as sulphonic acids. When, upon further addition of sulphuric acid, the latter remains colorless, the volume of the undissolved oil, which consists of paraxylol and aliphatic hydrocarbons, is read off. Let this = *c*. The oil is now drawn off from the acid and shaken with an equal volume of fuming sulphuric acid, containing 20 per cent. anhydride. Paraxylol dissolves and the fatty hydrocarbons remain unattacked. If their volume = *d*, then the difference, *c*-*d*, will yield the amount of paraxylol present.

If the sums of the volume percentages of meta- and paraxylol and the aliphatic hydrocarbons be added, and their sum subtracted from 100, the difference will represent orthoxylol.

### 3. Crude Anthracene.

The determination of anthracene by the method of Luck (modified by Meister, Lucius and Brüning) depends on the property of anthracene to yield anthraquinone on oxidation with chromic acid in acetic acid solution. The latter compound is not attacked by further action of chromic acid and of sulphuric at 100°. On the contrary, the other constituents of anthracene (acenaphthene, fluorene, phenanthrene, carbozol, fluoranthene, etc.), are either completely destroyed or converted into sulphonic acids, which are soluble in water or alkalies. 1 gr. crude anthracene is covered with

45 c.c. glacial acetic acid in a 500 c.c. flask. The flask is provided with a double-bored stopper, through one opening of which a separatory funnel is inserted, while through the other there issues an adapter, which is connected with a condenser. To the boiling solution of anthracene, 15 grs. chromic acid in 10 c.c. glacial acetic acid and 10 c.c. water are gradually added. The chromic acid is added at intervals of 2 hours. The solution is boiled 2 hours, stood aside for 12 hours, diluted with 400 c.c. water, and after 3 hours is filtered from the separated anthraquinone. This is washed first with pure water, then with boiling alkali, and finally again with water. It is then rinsed from the filter into a small flat porcelain dish. The water is evaporated, and the residue, after being dried at 100°, is heated on a water-bath with 10 times the volume of fuming sulphuric acid (68° Bé.). The solution so obtained is allowed to stand for 12 hours in a moist place, is diluted with 200 c.c. cold water, and the pure anthraquinone formed is filtered off. The latter is washed as before, rinsed into weighed capsules, dried at 100° and weighed. Thereupon the anthracene is volatilized by heating, and any remaining ash is deducted from the weight first obtained. The anthraquinone so found is then calculated into anthracene. 207.5 anthraquinone = 177.58 anthracene.

#### 4. Crude Carbolic acid.

*Determination of phenol.*—120 grs. crude acid are distilled from a small bulb, which is attached to a condenser, until about 8 grs. remain.\* The distillate is dissolved in ether and shaken out with 10 per cent. caustic soda in a separatory funnel. The ethereal layer is washed several times with dilute alkali, and the aqueous layer is washed several times with ether. The united alkaline extractions are decomposed with hydrochloric acid (1 : 1), which is added to acid reaction, and extracted with ether. After the ethereal solutions have been washed with water and the acid liquid with ether in a separatory funnel, the ethereal solutions are placed in a weighed flask. The ether is distilled off as far as possible, and

\* This procedure is suitable because the subsequent extraction with ether is more easily accomplished, and a sharper separation of the two layers is obtained.

the last traces are removed by attaching the flask to a dephlegmator or Linnemann column and heating the same over a wire gauze until an inserted thermometer indicates above 100°. The contents are then allowed to cool and are weighed, together with the flask.

### 5. Dimethyl Aniline.

The approximate determination of monomethyl aniline can be accomplished by the rise in temperature on mixing with an equal volume of acetic anhydride.

Every degree rise in temperature corresponds to approximately  $\frac{1}{4}$  per cent. monomethyl aniline. On mixing pure dimethyl aniline with acetic anhydride, a depression of  $\frac{1}{2}^{\circ}$  is observed. Each test requires 4 c.c.

The monomethyl aniline may be more exactly determined by the method of Nöltning and Boasson by allowing nitrous acid to act on the product. Monomethyl aniline is thereby converted into ether-soluble methyl-phenyl-nitroso amine  $C_6H_5N(NO)(CH_3)$ , whereas dimethyl aniline hydrochloride is converted into the hydrochloride of nitroso dimethyl aniline  $C_6H_4(NO).N(CH_3)HCl$ , which cannot be extracted by ether from its aqueous solution. According to Nietzki, 30 grs. dimethyl aniline are dissolved in 80 grs. conc. hydrochloric acid and about  $\frac{1}{2}$  liter water. The solution is well cooled and 38 grs. sodium nitrite are run in. After a while the solution is repeatedly extracted with ether, the ethereal solutions are united, the ether is evaporated off, and the residual oil is dried over sulphuric acid and weighed. The nitroso amine found, when multiplied by .786, gives the monomethyl aniline originally present.

# Appendix.

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## A. White Paint (White Lead).

A WHITE paint consists of a white pigment ground in a suitable oil, usually linseed oil. A very common form, and for general uses the best, is that termed "white lead," which is essentially the pigment white lead  $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$  ground with linseed oil. Other pigments, not necessarily adulterants, which may be admixed or *per se* are barium sulphate, lead sulphate, zinc oxide, zinc carbonate, zinc sulphide, strontium sulphate, calcium sulphate, calcium carbonate, magnesite, kaolin and silica. These and others are brought into the market in one form or another under various names. Mineral oils, rosin oil, etc., may be present with the drying oil of the paint. These may be detected, after separation from the pigment, by other methods given in the chapter on Oils.

### Analysis.

In a small Erlenmeyer flask about 5 grs. paint are weighed out. This is repeatedly washed by decantation with pure ether until a few drops of the latter leave no non-volatile residue on evaporation. The residue is thrown on a filter or else freed from adhering traces of ether by a current of air. The collected ethereal extractions are evaporated, and, after expelling the last traces of ether in the usual way, the residual oil is weighed, and if necessary examined. The weight of the residue is gotten by difference. It is then subjected to analysis by the following scheme (see table on page 170).

The residue may contain  $\text{PbSO}_4$ ,  $2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$ ,  $\text{BaSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{ZnCO}_3$ ,  $\text{ZnO}$ ,  $\text{SiO}_2$ , clay, etc. It is covered with hot acetic acid, diluted, heated and filtered.

## B. Manganese Dioxide, Bleaching Lime, Etc.

The simplicity of the Lunge nitrometer (Fig. 1) and its principle furnish a more extended use of the same in quantitative an-

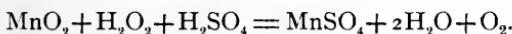
1. <i>Residue</i> may contain $\text{SiO}_2$ , clay, $\text{PbSO}_4$ , $\text{CaSO}_4$ , $\text{BaSO}_4$ . Filter and contents are transferred to a small beaker and are digested for 12 hours with a saturated solution of ammonium carbonate. Substance is then filtered and thoroughly washed. This filtrate is discarded. The residue on the filter is treated with hot acetic acid, filtered and thoroughly washed.	a. <i>Filtrate</i> may contain zinc, lead, barium and calcium salts. It is saturated with hydrogen sulphide, filtered and washed with hydrogen sulphide water.	b. <i>Residue</i> . $\text{PbS}$ , $\text{ZnS}$ . It is treated with nitric acid and evaporated with boiled off. $\text{HCl}$ is added, followed by sulphuric acid conc., until vapors of the dilute $\text{H}_2\text{SO}_4$ to precipitate barium. It is cooled and water is added. It is filtered and ppt. is washed.	c. <i>Filtrate</i> . Hydrogen sulphide is added, followed by $\text{HCl}$ is added, until the latter evolves. It is cooled and water is added. It is filtered and washed.	d. <i>Residue</i> . This is dried, ignited, and $\text{N}_2\text{H}_4\text{OII}$ is added to alkaline reaction solution is allowed to stand, filtered, and calculated to $\text{BaCO}_3$ .	e. <i>Filtrate</i> . This is dried, ignited, made alkaline with weighed as $\text{BaSO}_4$ sodium carbonate, and calculated to $\text{BaCO}_3$ .	f. <i>Residue</i> is dried, ignited, and $\text{N}_2\text{H}_4\text{OII}$ is added to stand, filtered, and $\text{BaCO}_3$ .
2. <i>Residue</i> may contain $\text{BaSO}_4$ , $\text{SiO}_2$ . 3. <i>Filtrate</i> may contain lead acetate and calcium acetate. It is saturated with water and filtered.						
4. <i>Residue</i> may contain barium, carbon, silica and to a porcelain crucible. $\text{HNO}_3$ is dissolved in di-peatedly taken to added and warmed, added, allowed to stand, dried, with $\text{HCl}$ , $\text{H}_2\text{SO}_4$ is added, and is taken up with evaporated until hours, filtered, ignited, and water and latter evolves, nited over a blast furnace, formed is and weighed, as $\text{PbSO}_4$ , filtered, washed $\text{CaO}$ , it is calcuated to $\text{CaSO}_4$ , and weighed.	5. <i>Filtrate</i> may contain barium, carbon, silica and to a porcelain crucible. $\text{HNO}_3$ is dissolved in di-peatedly taken to added and warmed, added, allowed to stand, dried, with $\text{HCl}$ , $\text{H}_2\text{SO}_4$ is added, and is taken up with evaporated until hours, filtered, ignited, and water and latter evolves, nited over a blast furnace, formed is and weighed, as $\text{PbSO}_4$ , filtered, washed $\text{CaO}$ , it is calcuated to $\text{CaSO}_4$ , and weighed.	6. <i>Residue</i> may contain $\text{PbS}$ , transferred to a porcelain crucible. $\text{HNO}_3$ is ammonium oxalate is added. Ammonium oxalate is weighed as $\text{PbCO}_3$ , due is determined after ignition as $\text{Pb(OH)}_2$ . $\text{Pb(OH)}_2$ is added, allowed to stand, dried, and calcuated to $\text{PbCO}_3$ .	7. <i>Filtrate</i> con. is dried, ignited, made alkaline with weighed as $\text{PbSO}_4$ sodium carbonate, and calculated to $\text{PbCO}_3$ .	8. <i>Residue</i> due is ignited, weighed as $\text{SiO}_2$ , may contain alumina, it is ppt. with ammonia, filtered, ppt. is ignited and weighed as $\text{Al}_2\text{O}_3$ .	9. <i>Filtrate</i> due is ignited, weighed as $\text{SiO}_2$ , may contain alumina, it is ppt. with ammonia, filtered, ppt. is ignited and weighed as $\text{Al}_2\text{O}_3$ .	
BaSO <sub>4</sub> ,	SiO <sub>2</sub> ,	Al <sub>2</sub> O <sub>3</sub> ,	PbSO <sub>4</sub> ,	CaSO <sub>4</sub> ,	$\text{zPbCO}_3$ , Pb(OH) <sub>2</sub> ,	ZnO, ZnS,
						CaCO <sub>3</sub> .

\* When much lime is present the separation is not complete. For closer investigation consult Friedheim, "Leitfaden für die quantitative chemische Analyse," p. 228; Clasen, Smith Quantitative Analysis, p. 27.

alysis. In fact a quantitative method is insured wherever, under convenient conditions, an equivalent in form of gas is evolved by the chemical decomposition of a substance. Such substances are manganese dioxide, bleaching lime, hydrogen peroxide, etc., etc. For the purpose of the estimation of their value either the original nitrometer (Fig. 1), or, even more convenient, the later form of gasvolumeter, may be used. A slight modification, a generator similar in principle to that in Fig. 9, is used. A plain, thick, wide-necked bottle, with a perforated, well-ground stopper, which is provided with a small internal receiver, is connected with the opening in the stopcock (Fig. 1) by the stout rubber tube. Since the volume read off is displaced air, the zero point taken need not necessarily be the zero mark on the apparatus. The apparatus is adjusted as usual, and the readings are reduced to  $0^{\circ}$  C. 760 mm. pressure. Decomposition is complete in the generator when in agitating the latter the mercury meniscus does not change.

### 1. Manganese Dioxide.

When manganese dioxide, in very finely divided condition, and hydrogen peroxide are brought together in acid solution the decomposition which ensues is expressed by the equation



Since 1 c.c. oxygen at  $0^{\circ}$  C. 760 mm. weighs 1.43003 mg., every c.c. oxygen obtained when reduced to the same conditions will equal .00389 gr.  $\text{MnO}_2$ .

*Operation.*—About .19 gr. substance is placed in the generator, and shaken with dilute sulphuric acid in order to decompose any carbonates present. Somewhat more than 3.7 c.c. of a 2 per cent. hydrogen peroxide solution (*i.e.*, the theoretical amount for the above quantity of substance) are poured into the little cup which is placed in the generator. The mercury in both tubes is placed on the same level and read off. The cup on (*a*) and the side tube are put into communication when the generator flask is attached. The stopcock is then turned to establish communication between the eudiometer (*a*) and the generator, whereby no change in the mercury level must occur. The contents of the generator are then mixed, and after decomposition has taken place the mur-

cury\* levels are again adjusted, the apparatus is allowed to stand for a while,† the volume is read off, reduced, and calculated into manganese dioxide by means of the above data.

## 2. Bleaching Lime.

Reaction takes place between bleaching lime and hydrogen peroxide as follows :



Therefore every volume of oxygen evolved represents an equal volume of "active" chlorine in the bleaching lime. The latter is prepared for use as usual by weighing 7-8 grs. in a weighing bottle. The contents are poured into a porcelain mortar, rubbed to a thick paste, diluted with water to a thin paste and poured into a liter flask through a funnel. The flask is filled to the mark. 40-50 c.c. of this turbid solution are used. The hydrogen peroxide, which is placed in the little cup, is first made alkaline by careful addition of sodium hydrate. The operation is conducted as above.

## 3. Hydrogen Peroxide and Permanganate.

Since  $5 \text{ H}_2\text{O}_2 + 2 \text{ KMnO}_4 + 3 \text{ H}_2\text{SO}_4 = 8 \text{ H}_2\text{O} + \text{K}_2\text{SO}_4 + 2 \text{ MnSO}_4 + 5 \text{ O}_2$ , the value of either one or the other can be determined by using an excess of one or the other in the operation. Then every c.c. oxygen reduced to  $0^\circ \text{ C}$ . 760 mm. = 2.8243 mg.  $\text{KMnO}_4$  or 1.5194 mg.  $\text{H}_2\text{O}_2$ , as the case may be.

## C. Asphalt and Asphaltic Substances.

Under this heading may be understood natural bitumens, varying in physical properties from hard, resonant, vitreous masses to soft, sticky masses. The former are known under the technical name of asphalt, and the latter under the name of maltha. With more or less mineral matter, which, likewise, can vary in physical and chemical composition, they belong to the product which, when admixed with suitable constituents and subjected to various processes, form the basis of artificial paving. Little is known regarding the origin of these substances and the nature of their organic constituents.

\* Instead of mercury, a salt solution or water may be employed.

† As soon as temperature, etc., are uniform, on standing, hydrogen peroxide evolves oxygen.

A very exhaustive and interesting research is that of Clifford Richardson,\* who has shown that the bitumen proper consists of hydrocarbons of the series  $C_n H_{2n}$ , and probably of lower series; that they contain very little, if any, oxygen, and that maltha is converted into asphaltum by reactions in which sulphur plays a prominent part. He has also subjected various isolated constituents to the usual processes of examination of oils, and has materially added to the data used in the analysis of asphalt.

A general description of analysis will be given, together with a few analytical results. The analysis includes the estimation of water, substances soluble in petroleum ether or petrolene, substances soluble in carbon bisulphide or turpentine, called asphaltene, organic matter not bitumen, and mineral matter. The method described and results appended are those of Laura A. Linton :†

(a) Water. 2-5 grs. substance, divided as finely as possible or spread over as large a layer as possible, are dried over sulphuric acid in a desiccator, or, better, in a current of dry air at a temperature not exceeding  $50^{\circ} C$ . The substance is reweighed, and the remaining results are based on anhydrous material.

(b) Petrolene. 2-5 grs. substance, depending on the amount of bitumen present, are weighed on a tared filter paper, which has been fitted into a much larger funnel, provided on its exit tube with a stopcock. The contents are repeatedly extracted with petroleum ether every few minutes. To remove the last traces digest several hours. The filter and contents and counterpoise are dried in a steam-bath and weighed. The loss in weight represents petrolene.

(c) Asphaltene. 1. The filter and contents are replaced on the funnel and extracted in a similar manner with turpentine. After complete exhaustion, which, at times, is tedious, the contents are washed with alcohol, dried and weighed as before. The difference represents asphaltene soluble in turpentine.

2. The process is repeated, using chloroform for extraction. The difference represents asphaltene soluble in chloroform.

The three fractions are summed up as "total bitumen."

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\* Journal Soc. Chem. Industry, Vol. xvii., p. 13 (1898).

† Journal Amer. Chem. Society, Vol. xvi., p. 809; Vol. xviii., p. 275.

(d) Mineral matter. The residue is ignited in a platinum dish, cooled and weighed. In case carbonates are present, the ash must be recarbonated by ignition with ammonium carbonate.

(e) Matter not bitumen is that which remains when the sum of the percentages obtained in *a*, *b*, *c* and *d* are deducted from 100.

	Petroleo.	Turpentine Fraction.	Chloroform Fraction.	Asphalting.	Total Bitumen.	Ratio of Chloroform Fraction to Bitumen.	Organic Matter not Bitumen.	Mineral Matter.
Trinidad asphaltum.....	35.40	12.3	5.29	17.59	52.99	1 : 10	10.96	36.1
Scyssel asphaltic rock (Eastern France)*.....	7.49	3.95	.37	4.32	11.8	1 : 31		88.2
Sandstone† asphaltic rock (locality unknown).....	5.12		2.27	2.27	7.39		.75	91.86

## D. Food Stuffs.

Under this head will be considered a few types of food stuffs, such as milk, flour, coffee and pepper. Armed with the general methods it is quite possible, using such modifications and precautions as good judgment dictates, to conduct the investigation of other substances.

### 1. Milk.

1. The average composition of new cow's milk is :

Fat.	Casein.	Albumin.	Milk Sugar.	Ash.	Solids.	Water.
3.50	3.98	.77	4.00	.17	13.13	86.87

Its average specific gravity is 1.029-1.039.

2. Products made from cow's milk may contain one, several or all of these constituents, with or without necessary additions. They depend on the operation which the milk undergoes, and the nature and quantity of material added to yield the products desired. Under this head come : *a*. Cream, skim-milk, buttermilk, curd, whey, butter, cheese, milk sugar, casein, koumiss. *b*. Condensed milk, preserved milk, lactated foods.

\* This belongs to the class of asphaltic limestones, and can contain as much as 91.3 per cent. calcium carbonate.

† Analysis by author.

3. Finally, milk may contain alteration products, such as lactic acid, etc., and preservatives, such as borax, salicylic acid, bicarbonate of soda, ultramarine, etc. Practically, the main adulterant used is water.

A description of an analysis embracing all these substances is for the present purpose too extended.

For a complete analysis of milk the following apparatus should be prepared, and if possible all parts of the analysis should be conducted at once :

1. Sp. gr. hydrometer, hydrostatic balance or pyknometer.
2. Porcelain or platinum capsule of about 50 c.c. capacity, weighed together with ignited bar-sand and a small glass rod.
3. Small weighed platinum dish or crucible.
4. A weighing bottle of convenient form and two separately dried and weighed filter papers.

*Operation.*—The specific gravity is taken at 15.5° C. = 60° F.

(a) Solids. 10 c.c. milk, the weight of which is equal at 15.5° C. to the sp. gr. with the decimal point moved one place to the right, are placed in the platinum dish with the sand, are evaporated to dryness with occasional stirring on a water-bath, and are finally dried at 105° in an air-bath to constant weight.

(b) Ash. The contents of the second crucible, 10 c.c., are evaporated to dryness, incinerated and weighed. In more exact work the dry mass is simply charred, washed with water and filtered. After incinerating the charred mass, the washings are added and evaporated to dryness. In this case volatile portions, such as salt, are retained.

(c) Fat, casein and albumin. Hoppe-Seyler method. 10 c.c. milk are diluted to 50 c.c. in a small beaker with water. The solution is warmed to 45° and 1-2 c.c. of 10 per cent. acetic acid are added. Casein and fat are precipitated in form of curd, whereas albumin remains in solution. The precipitate is filtered on a weighed filter, dried at 105° in a weighing bottle and reweighed. The weight of bottle + filter deducted from the latter weight gives the weight of casein and fat.

The filter is placed in a suitable form of extractor,\* which is put

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\* The Thorn extractor is very suitable.

into operation for 6-8 hours. The filter and contents are then placed in a perfectly clean weighing bottle, dried at  $105^{\circ}$ , and reweighed. Bottle plus filter plus casein minus bottle plus filter gives the weight of casein. Casein plus fat minus casein = fat. The filtrate containing albumin is boiled for several minutes. The precipitate formed is collected in another weighed filter, is washed, dried and weighed.

(d) Milk sugar. Ritthausen method. 10 c.c. milk are diluted to about 100 c.c. with water in a beaker of about 200 c.c. capacity. Everything except soluble salts and milk sugar is precipitated by the addition of 10 c.c. copper sulphate solution (69.28 grs. copper sulphate per liter) and sufficient sodium hydrate solution to incompletely precipitate the copper. The precipitate formed, together with liquid, is thrown on a ribbed filter of about 200 c.c. capacity, and filtrate and washings are collected in a 500 c.c. flask and diluted to the mark. 200 c.c. filtrate are boiled with 25 c.c. each of Fehling's solutions for 6 minutes and the cuprous oxide formed is treated as on page 86. The milk sugar is found by reference to the following table:

*Table for Milk Sugar.*

Weight of Copper, mg.	Milk Sugar. mg.	100 Parts of Milk Sugar Precipitate of Copper Oxide.	Reduction Ratio.
392.7	300	130.9	I : 7.43
363.6	275	132.2	I : 7.50
333.0	250	133.2	I : 7.56
300.8	225	133.7	I : 7.59
269.6	200	134.8	I : 7.65
237.5	175	135.7	I : 7.70
204.0	150	136.0	I : 7.72
171.4	125	137.1	I : 7.78
138.3	100	138.3	I : 7.85

All weights of constituents are calculated into per cent.

For very many purposes only one or two of these constituents are wanted. In the technical analysis of milk, adulteration with water and by skimming are guarded against by estimation simply of specific gravity, total solids and fat. Necessarily quicker and shorter methods are required. For the estimation of fat the method

of Leffmann-Beam\* and Chevalier† are there substituted. These, however, require special forms of apparatus.

Albuminoids may be determined by the Kjeldahl (see p. 74) or some modified method, such as the Gunning method (see p. 182), or by combustion with soda-lime (see p. 74). In any case nitrogen is calculated from ammonia obtained, and is multiplied by the factor 6.25 to obtain total albuminoids.

*Condensed milk.*—This may or may not contain cane sugar. The latter is a common form and contains about 25.51-30.05 per cent. water, 6.60-10.08 per cent. fat, 44.47-53.27 per cent. cane and milk sugars, 10.11-12.04 per cent. casein, and 1.80-2.09 per cent. salts.‡ For analysis, definite portions are diluted and analyzed as heretofore. Cane sugar will be present with the milk sugar, and may, if necessary, be determined after inversion. (See p. 86.)

## 2. Butter.

*Butter* consists of butter fat, curd, water, milk sugar and salt. A complete analysis is conducted as follows:

About 5 grs. uniform sample are weighed, together with a suitable weighing bottle, which has previously been weighed. A short glass rod, flattened at one end, is weighed in also. With this improvised spatula, about half the butter is placed on a tared filter paper and extracted with chloroform in an extractor. The weighing bottle, spatula and remaining butter are reweighed, and the quantity used is gotten by difference. The quantity, number 2, remaining in the bottle is also calculated.

(a) Fat. Quantity 1 is extracted for a period of about 6 hours with chloroform. The curd, milk sugar and salt, plus filter paper, are dried and weighed, and their combined weight, deducted from quantity 1, gives fat, plus water, which is calculated into per cent. In order to obtain the percentage of fat, the water percentage found in (c) is deducted.

(b) Curd, salt and milk sugar. The residue on the filter consists of milk sugar, salt and curd. It is washed with hot water and the collected washings are diluted to a definite volume. Aliquot

\* Leffmann-Beam Milk Analysis.

† Becke, Milch Prüfungs-Methoden, p. 40.

‡ Battershall, Food Adulterations and Its Detection, p. 53.

portions are used for milk sugar (see above) and salt (p. 177) determinations. The filter, plus curd, is dried at 105° and reweighed. The curd is found by deducting the weight of filter paper from the above weight.

(c) Water. Quantity 2 is dried to constant weight.

All results are calculated to percentage.

*Examination of butter fat* is most important, as this is the only means of distinguishing genuine butter from substitutes. For this purpose the filtered fat is used, and the constants determined are viscosity.\* Reichert-Meissl number, p. 117; iodine number, p. 111; Köttstorfer number, p. 110. The behavior in the refractometer is also a valuable criterion. For constants see p. 113.

### Tea, Coffee and Cocoa.

The analysis of genuine tea and coffee is rarely conducted for the purpose of determining their values as producers of beverages. On the other hand, the estimation of caffeine in the manufacture of that substance and the disclosure of foreign admixtures of organic nature, foreign leaves in the case of tea, foreign and artificial beans in the case of coffee, coloring matter (facings), Prussian blue, turmeric, indigo, etc., and of substances of inorganic nature, mineral matter, weighting material, etc., often demand investigation of chemical and microscopic nature.†

### 3. Tea.

The analysis of twenty-three teas in Russian commerce by Dragendorf gave a mean :

	Per cent.
Water,	10.00
Extract,	32.67
Theine, caffeine,	1.90
Tannin (four determinations),	11.42
Ash,	6.23

(a) Moisture. 1-2 grs. powdered sample are dried to constant weight in a weighing bottle.

(b) Extract. 5 grs. sample are boiled with 500 c.c. water for one hour on a reflux condenser. An aliquot portion is drawn off,

\* Dr. Neuman Wender, Journal Amer. Chem. Society, Vol. xvii., p. 719.

† Foods, Composition and Analysis. A. W. Blyth.

evaporated to dryness and weighed. Adulteration with spent leaves lowers the percentage of extract. The determination is not very reliable, because genuine tea can contain from 26–40 per cent. extract.

(c) Theine, caffein. 5 grs. sample are boiled on a reflux with water for several hours. The liquid and leaves are evaporated with some magnesia to pasty condition. This is exhausted with chloroform, and the latter is separated and distilled off. The residue is dissolved in a little boiling water, evaporated to dryness at a gentle heat, and weighed.

(d) Tannin. The process (p. 149) may be employed.\*

(e) Ash. 1–5 grs. sample are incinerated in a platinum dish. There is no danger of volatilization since the leaves readily incinerate at low temperatures. The ash is cooled and weighed. It should equal 5.17–7.02 per cent. It is lixiviated with hot water, and the soluble portion is removed by filtration on an ashless filter. Filter and contents are replaced in the dish, ignited, cooled and weighed. The insoluble portion is gotten directly, and the soluble portion is obtained by difference. The former should be 2.64–4.22 per cent. and the latter 1.33–2.87 per cent. Another characteristic is about 1 per cent. manganous oxide.

#### 4. Coffee.

The analysis comprises the estimation of water, caffein, fat, fiber, ash. The following averages were obtained by König :

	Moisture.	Fat.	Fiber.	Ash.	Albuminoids.	Caffein.	Sugar.
Unroasted coffee.....	Per cent. 11.23	Per cent. 13.27	Per cent. 18.17	Per cent. 3.92	Per cent. 12.07	Per cent. 1.21	Per cent. 8.55
Roasted coffee.....	1.15	14.48	19.89	4.75	13.98	1.24	.66 { Telus gums and dextrin.

Water, ash and caffein are estimated as in tea.

(a) Fat. 2–3 grs. finely powdered sample are placed in an

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\* A more reliable method is that of Councill and Schroeder, Zeit. fur anal. Chem., 25, 121.

extractor with petroleum ether and extracted for several hours. The petroleum ether is distilled off, and the residue, which is quite pure, is dried and weighed.

*Fiber.*\*—2 grs. substance are washed several times by decantation with ether and boiled for  $\frac{1}{2}$  hour on a reflux with 200 c.c. 1.25 per cent. sulphuric acid in an Erlenmeyer flask. The solution is filtered through linen, and the filtrate is refiltered through a Gooch crucible. The two residues are washed, reunited and boiled in the same flask with 200 c.c. 1.25 per cent. caustic soda. Filtration and washing are conducted as before. The contents of the linen are washed with alcohol into the crucible and then washed with ether, dried at  $110^{\circ}$  and weighed. It is then incinerated and the ash is deducted. Adulterants may be inorganic coloring matter, etc., in which case, the percentage and nature of the ash would give some indication. Organic adulterants consist of artificial beans, which are usually made of flour, chicory and sugar caramel, which forms on the roasted bean when the unroasted bean is treated with sugar solutions. Roughly, the presence of the first named may be detected by covering the sample with water. Natural beans float, whereas artificial beans sink. The test is not always conclusive. The coffee bean contains no starch, and therefore flour in any form can be recognized by the starch reaction. Chicory may be suspected when the ash contains much over .03 per cent. chlorine. Careful incineration is advised in this case. Burnt sugar or caramel is detected by the rapid darkening of water on which a little coffee is sprinkled. Comparative microscopic examinations afford the safest clues.

### 5. Cocoa and Chocolate.

Cocoa, the ground product of the decorticated cocoa bean, forms the basis of all cocoa preparations. The average composition, according to J. A. Wanklyn, is :

	Per cent.
Fat (cocoa butter), . . . . .	50.00
Theobromin, . . . . .	1.50
Starch, . . . . .	10.00
Albumin, etc., . . . . .	18.00
Gum, . . . . .	8.00
Coloring matter, . . . . .	2.60
Water, . . . . .	6.00
Ash, . . . . .	3.60

\* U. S. Dept. Agriculture Bulletin, No. 13.

When incorporated with refined sugar it forms chocolate. Frequently the expressed and "defatted" substance is used for the above. Both varieties, mixed with various kinds of starch, sugar and flavoring extracts, constitute cocoa preparations. In soluble cocoa preparations the former is previously defatted, treated with ammonia to destroy the cellular structure, and then with necessary reagents to transform the albuminoids to a soluble form.

The use of the above substances in moderation is for many reasons allowable, but their abuse is considered adulteration. Mineral matter, weighting material, etc., may be present as adulterants.

The analysis embraces the determination of water, fat, starch, theobromin, sugar, nitrogenous matter and ash.

(a) Water. 2-5 grs. rasped or powdered sample are dried to constant weight at  $105^{\circ}$ .

(b) Fat. 2 grs. rasped or powdered sample are, if necessary, mixed with sand and extracted with ether. The ether is distilled off and the fat is dried at  $100^{\circ}$  and weighed. If previous "defatting" and addition of foreign fat be suspected, the usual constants are determined. The iodine number of genuine cocoa butter is about 34, Köttstorfer's about 200.

(c) Sugar. The residue from (b) is extracted with cold water and an aliquot portion is inverted. The remaining operation is as on p. 86.

(d) Starch. The residue from (c) is boiled with water and inverted. In an aliquot portion of the solution the starch is determined as in p. 99. To determine the nature of the starch a microscopic examination is necessary.

(e) Theobromin is determined as under theine, caffein (p. 179), except that the sample is first defatted with petroleum ether and the final extraction is done with boiling 80 per cent. alcohol. The residue left on expelling the latter is, if necessary, purified with petroleum ether, dried and weighed.

(f) Nitrogenous matter is determined by the Kjeldahl process, p. 74.

(g) Ash. 5 grs. sample are incinerated in a platinum dish and weighed. The fact that the dry cocoa bean contains about 1.5 per cent. of phosphoric acid is of importance.

**6. Flour and Other Cereals.**

The analyses comprise the determination of water, ash, starch, fat, nitrogenous matter, water extract and wood fiber. Adulterants would mainly be present in form of inorganic weighting material.

(a) Water. 2-5 grs. sample are dried at  $105^{\circ}$  to constant weight.

(b) Ash. 2-5 grs. sample are incinerated in a platinum dish, cooled and weighed. Frequently the ash is difficult to free from carbon particles. In this case careful addition now and then of crystals of pure ammonium nitrate aids the incineration.

(c) Starch is determined after inversion, as usual. (See p. 99.) From the copper obtained, that produced by inversion of a cold water extract of an equal amount of flour must be deducted. The difference is then calculated into starch.

(d) Nitrogenous matter, which consists mainly of glutin, is determined as on p. 74, or by a modification known as the Gunning method. This differs only in the process of decomposition, which requires heating with 30-40 c.c. of a semi-fluid mass, obtained by warming two parts conc. sulphuric acid and one part ground potassium sulphate. The liquid is heated briskly until it becomes perfectly clear. In the remaining operation addition of sulphide of sodium is unnecessary.

(e) Fat. 5 grs. dried sample are extracted with ether in an extractor, and after expulsion of the latter the residue is dried and weighed.

(f) Water extract. 10 grs. flour are covered with 500 c.c. water and briskly shaken. 250 c.c. are filtered into a platinum dish, evaporated to dryness, dried and weighed. The residue, which contains sugar, gum, dextrin, albumin and phosphate of potash, should equal about 5 per cent. On ignition it should consist entirely of potassium phosphate. In a portion of the liquid, corresponding to the flour used in the starch determination, the reducing power in copper units is determined after inversion. (See e.)

(g) Wood fiber. The determination is of more use in the analysis of whole or crushed cereals. The determination is conducted as on p. 180.

The percentage values of wheat flour are by no means constant. 100 parts, according to Wanklyn, contain: water 16.5 per cent., fat 1.2 per cent., glutin, etc., 12.0 per cent., starch, etc., 69.6 per cent., ash .7 per cent.

### Spices, Etc.

Unless supplemented by a careful microscopic examination in the search for adulterants the chemical analysis of spices, etc., is of little value except in the matter of discovering the addition of inorganic substances, sand, etc. Water, ash, starch, fat (oils) and fiber determinations furnish the analytical data. The example selected is :

#### 7. Pepper.

Adulterations in form of various ground seeds, dust, sand, ground husks and shells, starch, flour, etc., etc., are found in cheaper grades.

- (a) Water. 2-5 grs. sample are dried at 105° and weighed.
- (b) Ash. The residue from the above is incinerated and weighed.
- (c) Starch. The substance is first washed with alcohol and then treated precisely as under starch (p. 99.) The solution is accurately neutralized and diluted to 500 c.c. before it is reduced with Fehling's solution.
- (d) Fats, etc. 1. Total ether extract.\* 2 grs. sample are extracted in a large Soxhlet apparatus with absolute ether for 24 hours. The extract is washed into a weighed capsule and the ether is allowed to evaporate spontaneously, but not too rapidly. It is then dried over night in a desiccator and weighed.

2. Volatile oil. The residue is heated to 110° for several hours and is reweighed. The difference represents volatile oil.

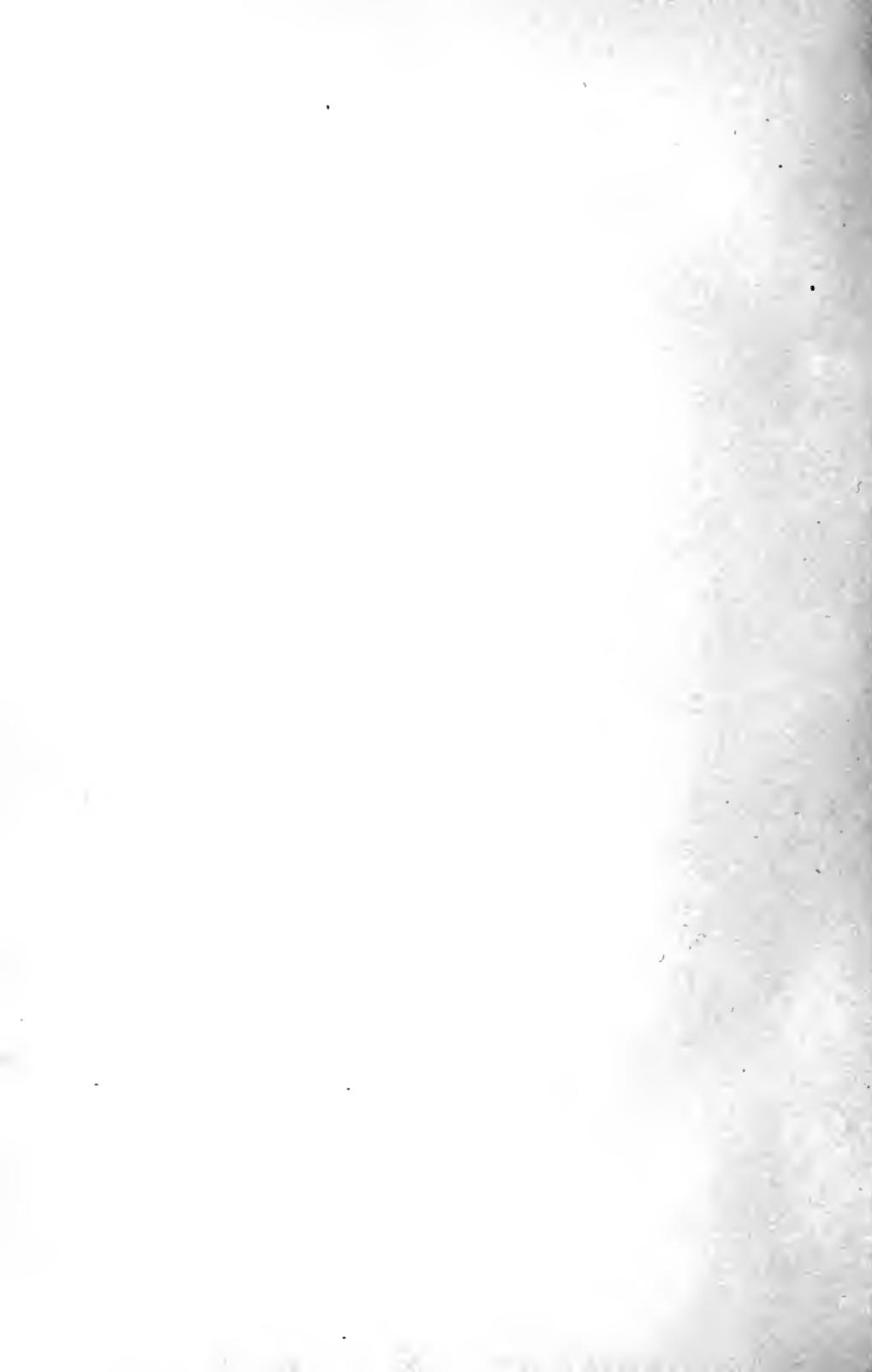
- (e) Fiber is determined as on page 180.

Black pepper is the dried unripe fruit of *piper nigrum*, and white pepper is the dried ripe fruit of the same deprived of its outer black covering. The following analyses† of both kinds in whole conditions will give a good basis of comparison :

	Water.	Ash.	Volatile Oil.	Ether Extract.	Starch.	Crude Fiber.
Whole black.....	8.15	2.91	1.48	8.68	33.92	8.74
Whole white.....	10.60	1.34	1.26	9.02	43.10	4.20

\* U. S. Dept. Agriculture Bulletin No. 13, p. 165.

† Bulletin loc. cit.



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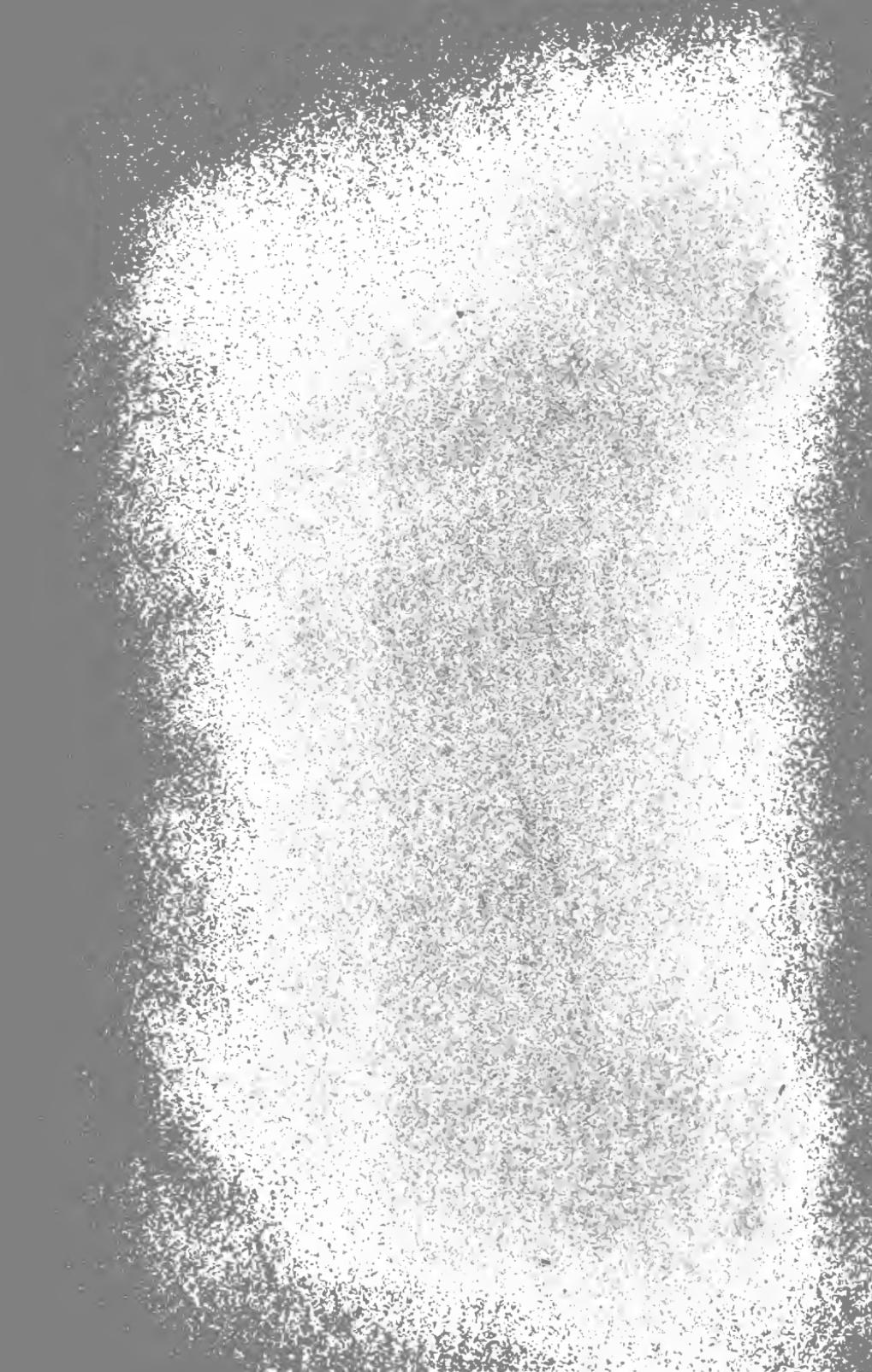
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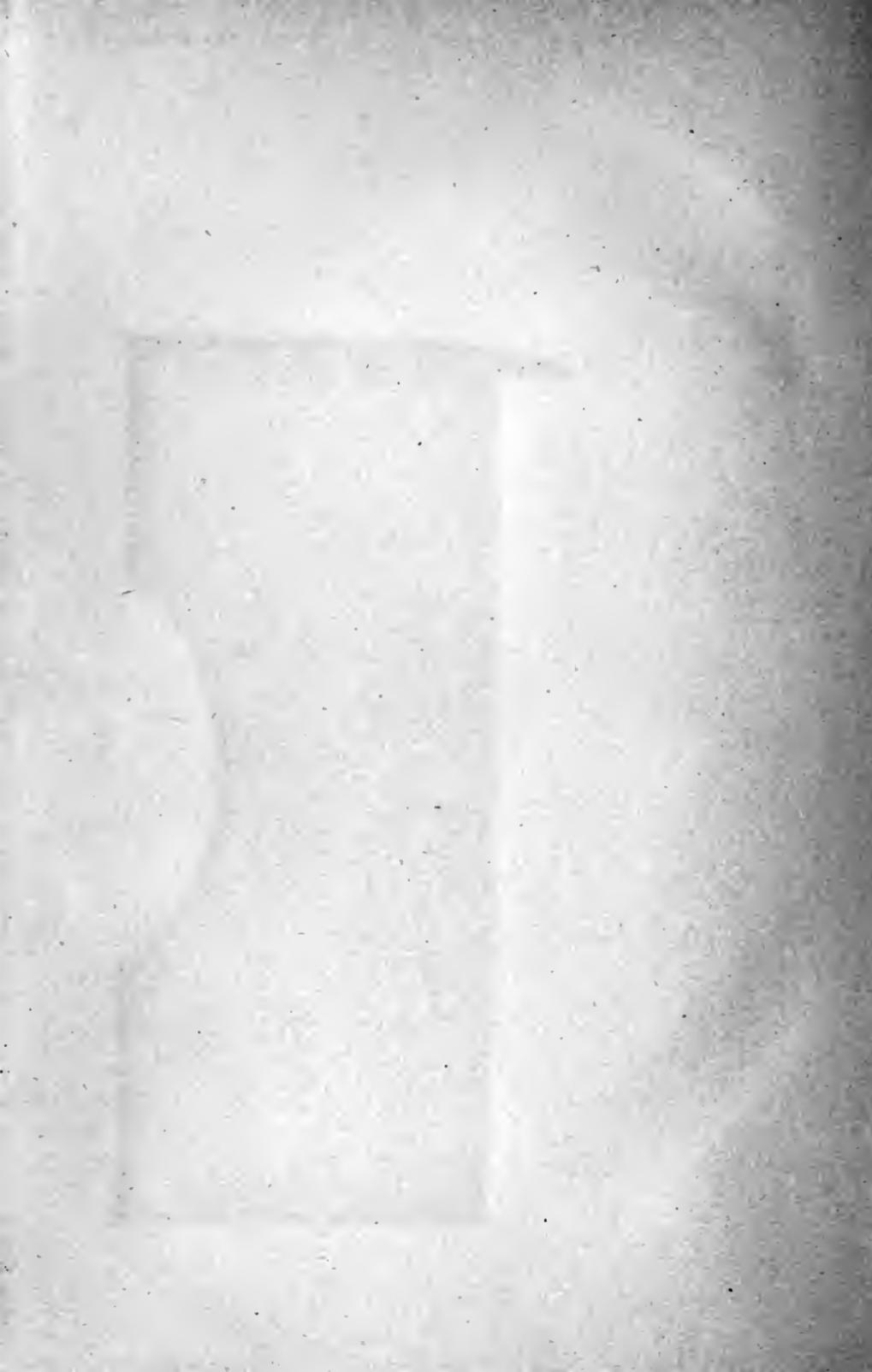
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